# Quantum Chemistry

Lecture 16

Implementation of Hartree-Fock Theory

NC State University

# The linear combination of atomic orbitals (LCAO)

Calculations of the energy and properties of molecules requires hydrogen-like wave functions on each of the nuclei. The Hartree-Fock method begins with assumption That molecular orbitals can be formed as a linear combination of atomic orbitals.

$$\Psi_i = \sum_{\mu=1}^{N} c_{\mu i} \phi_\mu$$

The basis functions $\phi_\mu$ are hydrogen-like atomic orbitals that have been optimized by a variational procedure. The HF procedure is a variational procedure to minimize the coefficients $C_{\mu i}$.  Note that we use the index m for atomic orbitals and i or j for molecular orbitals.

# Common types of atomic orbitals

Slater-type orbitals (STOs)

$$\phi_\mu \propto e^{-\zeta r}$$

The STOs are like hydrogen atom wave functions. The problem with STOs arises in multicenter integrals. The Coulomb and exchange integrals involve electrons on different nuclei and so the distance r has a different origin.
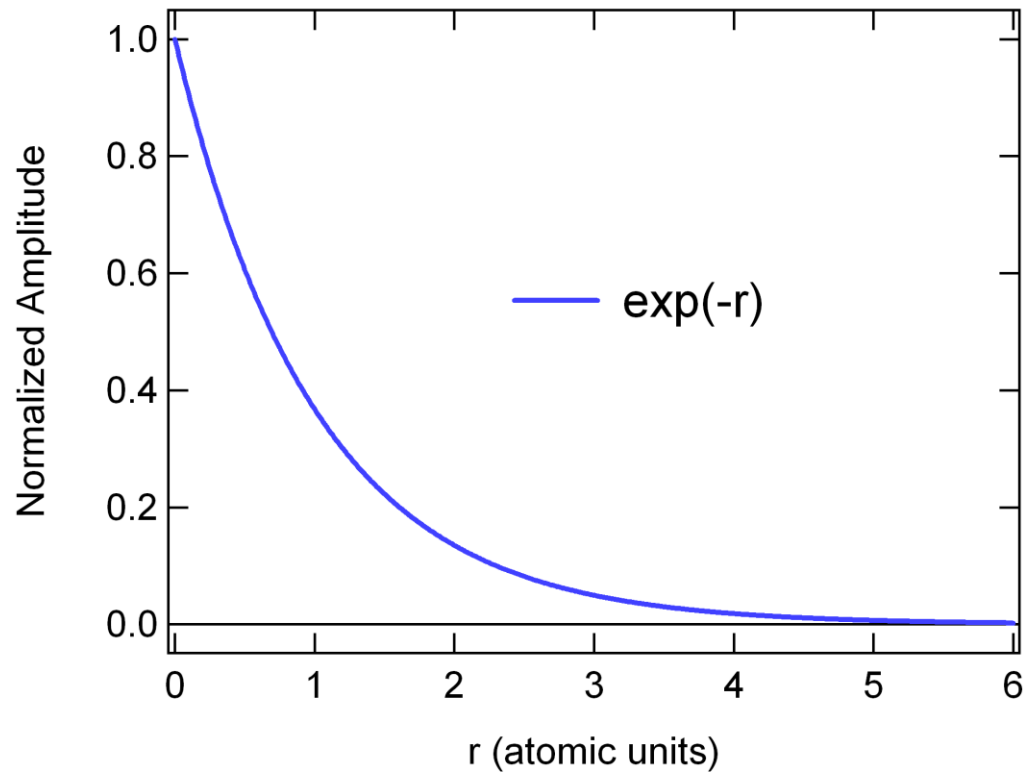
Gaussian-type orbitals (GTOs)

$$\phi_\mu \propto e^{-\alpha r^2}$$

Gaussian orbitals can be used to mimic the shape of exponentials, i.e. the form of the solutions for the hydrogen atom.  Multicenter Gaussian integrals can be solved analytically.
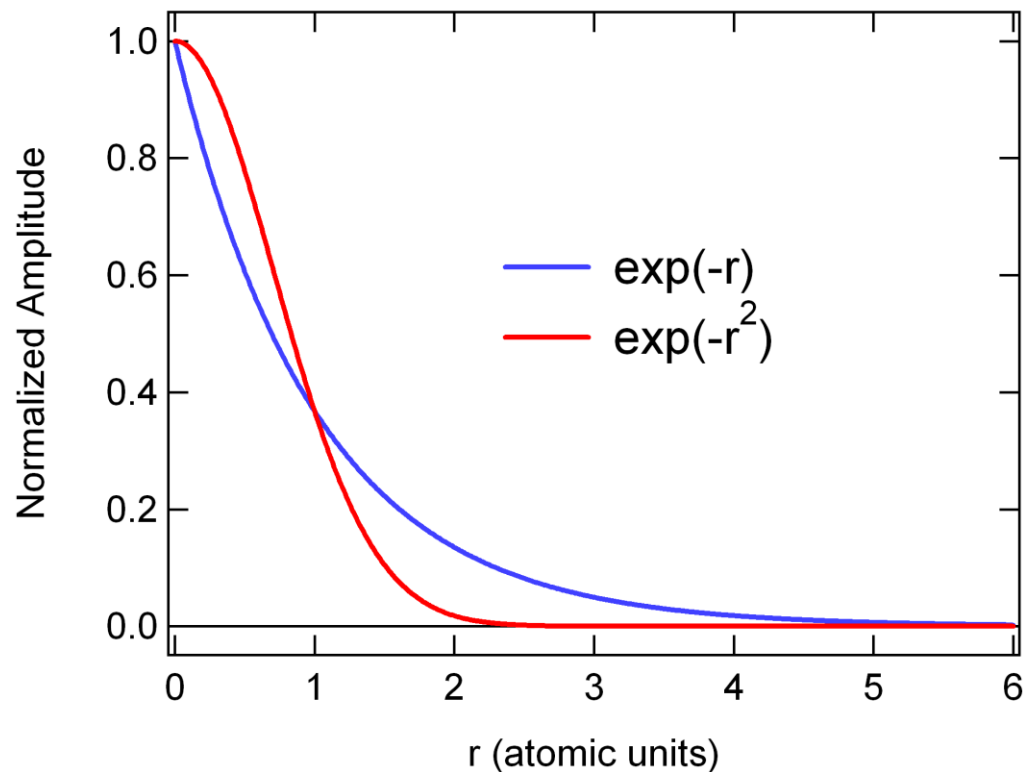
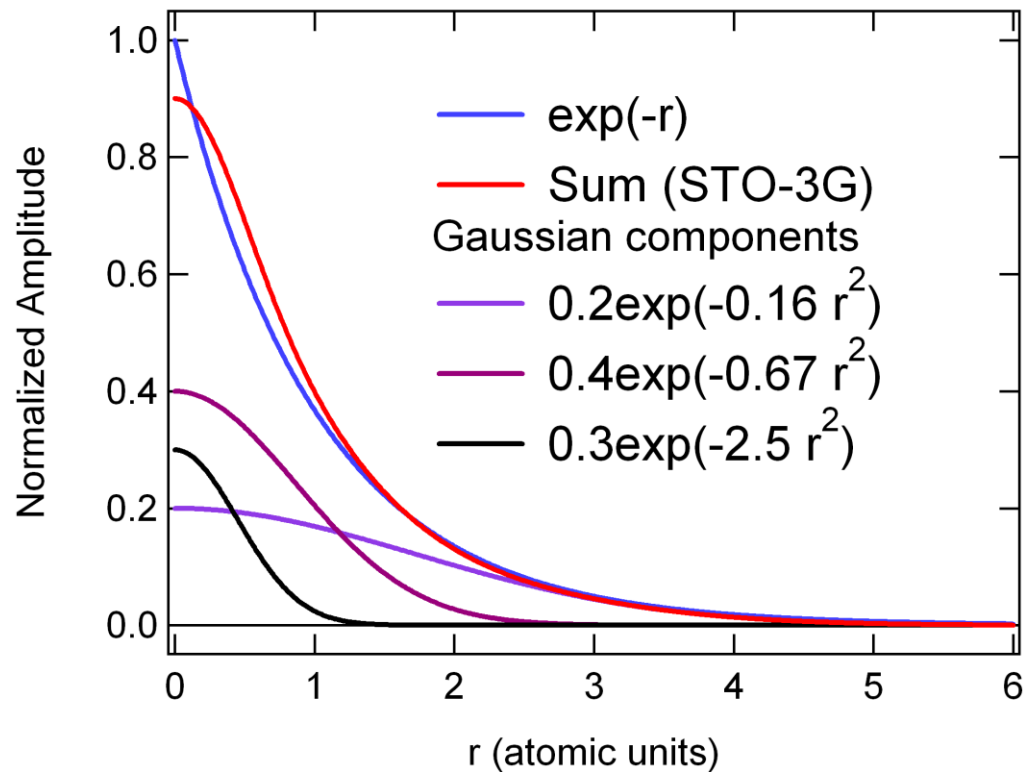# STOs vs GTOs

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GTOs are mathematically easy to work with, but the shape of a Gaussian is not that similar to that of an exponential.

# STOs vs GTOs

Therefore, linear combinations of Gaussians are used to imitate the shape of an exponential.  Shown is a representation of the 3-Gaussian model of a STO.



Legend:
- exp(-r)
- Sum (STO-3G)

Gaussian components
- $0.2\exp(-0.16\,r^2)$
- $0.4\exp(-0.67\,r^2)$
- $0.3\exp(-2.5\,r^2)$

Axes: Normalized Amplitude vs r (atomic units)

# Double-zeta basis sets

Since the remaining atoms have a different exponential dependence than hydrogen it is often convenient to include more parameters.

$$\phi_\mu = D_{\mu a} e^{-\zeta_a r} + D_{\mu b} e^{-\zeta_b r}$$

The second exponential is a diffuse function. It accounts for properties of a valence electrons involved in bonding.

When GTOs are used there are always multiple Gaussians required because the shape of Gaussians must be matched as closely as possible to that of exponentials. In a double-zeta basis there may be up to 3 Gaussians used to represent the first exponent $\zeta_a$ and 1 for the second exponent $\zeta_b$. In a so-called 6-31G basis set in the GAUSSIAN program, there are 6 Gaussians for core electrons and then 3 for $\zeta_a$ and 1 for $\zeta_b$.

# Application of the Variational Method to Fock Equations

# The variation procedure applied to the HF wave functions

The HF procedure uses the variational method to obtain the value of parameters that minimizes the energy

$$E = \langle \Psi | H | \Psi \rangle = \sum_{\mu\nu} c_\mu^* c_\nu \langle \phi_\mu | H | \phi_\nu \rangle$$

subject to the constraint the wave functions remain orthogonal

$$\langle \Psi | \Psi \rangle - 1 = \sum_{\mu\nu} c_\mu^* c_\nu \langle \phi_\mu | \phi_\nu \rangle - 1 = 0$$

The minimization of an equation subject to a constraint is carried out using the method of LaGrange undetermined multipliers.

$$\mathcal{L} = \langle \Psi | H | \Psi \rangle - E(\langle \Psi | \Psi \rangle - 1)$$

Note that the multiplier is the energy E and it will be determined during the procedure.

# The variational method in HF

Including the basis of atomic orbitals the LaGrangian can be written as:

$$\mathcal{L} = \sum_{\mu\nu} c_\mu^* c_\nu \langle \phi_\mu | H | \phi_\nu \rangle - E \left( \sum_{\mu\nu} c_\mu^* c_\nu \langle \phi_\mu | \phi_\nu \rangle - 1 \right)$$

In the variation method we are looking for the wave function $\phi$ that will minimize the energy. Here the condition is that the variation in the energy $\delta E = 0$ as indicated on the previous slide. This condition assures that E is stationary. A stationary point is usually a minimum. The differential is:

$$\delta\mathcal{L} = \delta\langle \Psi | H | \Psi \rangle - \delta\langle \Psi | \Psi \rangle E$$

# Conversion of the LaGrangian to a series of linear equations

The first variation in the Lagrangian is set equal to zero.

$$\delta \mathcal{L} = \sum_{\mu\nu} \delta c_\mu^* c_\nu \langle \phi_\mu | H | \phi_\nu \rangle - E \sum_{\mu\nu} \delta c_\mu^* c_\nu \langle \phi_\mu | \phi_\nu \rangle$$

$$+ \sum_{\mu\nu} c_\mu^* \delta c_\nu \langle \phi_\mu | H | \phi_\nu \rangle - E \sum_{\mu\nu} c_\mu^* \delta c_\nu \langle \phi_\mu | \phi_\nu \rangle = 0$$

Collecting the terms we have

$$\sum_\mu \delta c_\mu^* \left( \sum_\nu H_{\mu\nu} c_\nu - E S_{\mu\nu} c_\nu \right)$$

$$+\text{complex conjugate} = 0$$

# Expression of the matrix equations

This analysis leads to the matrix equations.

$$\sum_{\nu} H_{\mu\nu} c_{\nu} - E S_{\mu\nu} c_{\nu}$$

The explicit form of the matrix is:

$$\left(H_{11} - E_i S_{11}\right) C_{1i} + \left(H_{12} - E_i S_{12}\right) C_{2i} + \dots + \left(H_{1N} - E_i S_{1N}\right) C_{Ni} = 0$$

$$\left(H_{21} - E_i S_{21}\right) C_{1i} + \left(H_{22} - E_i S_{22}\right) C_{2i} + \dots + \left(H_{2N} - E_i S_{2N}\right) C_{Ni} = 0$$

....

$$\left(H_{N1} - E_i S_{N1}\right) C_{1i} + \left(H_{N2} - E_i S_{N2}\right) C_{2i} + \dots + \left(H_{NN} - E_i S_{NN}\right) C_{Ni} = 0$$

# The secular determinant

There are N equations and N + 1 unknown variables: $C_{1i}$, $C_{2i}$, $C_{3i}$, …, $C_{Ni}$, and $E_i$.
In order for the equations to have meaningful (non-zero) solutions they must comprise a secular determinant

$$\det A = \det \begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \dots \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \dots \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \dots \\ . & . & . \\ . & . & . \end{pmatrix} = 0$$

which leads to N eigenvalues, $E_i$ (i = 1,2,3,…N).
The solutions for the $\Psi_i = C_{1i}\phi_1 + C_{2i}\phi_2 + \dots C_{Ni}\phi_N$ under the constraint:

$$\sum_{\mu=1}^{N} \sum_{\nu=1}^{N} C_{\mu i} C_{\nu i} S_{\mu\nu} = 1$$

# Matrix representation

The fock hamiltonian is an effective one-electron hamiltonian

$$H^{eff}\Psi_i = E_i\Psi_i$$

$$AOs: \{\phi_1, \phi_2, \phi_3 \ldots \phi_N\}$$

$$MOs: \Psi_i = \sum_{\mu=1}^{N} c_{\mu i}\phi_\mu$$

The matrix representation for the overlap and interaction energies is:

$$S = \begin{pmatrix} S_{11}\ S_{12}\ S_{13}\ ...S_{1N} \\ S_{21}\ S_{22}\ S_{23}\ ...S_{2N} \\ ...\ ...\ ... \qquad ... \\ S_{N1}\ S_{N2}\ S_{N3}\ ...S_{NN} \end{pmatrix} \quad H = \begin{pmatrix} H_{11}\ H_{12}\ H_{13}\ ...H_{1N} \\ H_{21}\ H_{22}\ H_{23}\ ...H_{2N} \\ ...\ ...\ ... \qquad ... \\ H_{N1}\ H_{N2}\ H_{N3}\ ...H_{NN} \end{pmatrix} \quad C_i = \begin{pmatrix} C_{1i} \\ C_{2i} \\ ... \\ C_{Ni} \end{pmatrix}$$

# Eigenvalues are energies and eigenvectors are MOs

Thus, $\mathbf{H}C_i = E_i\mathbf{S}C_i$ Next, we define the matrices of coefficients and eigenvalues as:

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{13} & ...C_{1N} \\ C_{21} & C_{22} & C_{23} & ...C_{2N} \\ ... & ... & ... & ... \\ C_{N1} & C_{N2} & C_{N3} & ...C_{NN} \end{pmatrix}, \; E = \begin{pmatrix} E_{11} & 0 & 0 & ... & 0 \\ 0 & E_{22} & 0 & ... & 0 \\ ... & ... & ... & & ... \\ 0 & 0 & 0 & ... & E_{NN} \end{pmatrix}$$

Then the matrix form is $\mathbf{HC} = \mathbf{SCE}$. This system of equations is diagonalized if $\det|\mathbf{H} - \mathbf{ES}| = 0$. However, this is possible only in the MO basis.

AO basis: $\{\phi_1, \phi_2, \phi_3 ....\phi_N\}$

$S_{\mu\nu} = \langle\phi_\mu|\phi_\nu\rangle$: Not orthogonal

$H_{\mu\nu} = \langle\phi_\mu|H|\phi_\nu\rangle$: Not diagonal

MO basis: $\{\Psi_1, \Psi_2, \Psi_3 ....\Psi_N\}$

$\delta_{ij} = \langle\Psi_i|\Psi_j\rangle$: orthogonal

$E\delta_{ij} = \langle\Psi_i|H|\Psi_j\rangle$: diagonal

# The Roothan matrix procedure

The equations are solved on a computer using the Fock operator

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i}$$

which is solved for all of the basis functions (both occupied and unoccupied).  The coefficients obtained from this calculation are then used to calculate the Fock matrix whose elements are:

$$F_{\mu\nu} = \langle\chi_{\mu}|h|\chi_{\nu}\rangle + \sum_{\delta,\kappa} \left( \gamma_{\delta,\kappa} \langle\chi_{\mu}\chi_{\delta}|g|\chi_{\nu}\chi_{\kappa}\rangle + \gamma_{\delta,\kappa}^{ex} \langle\chi_{\mu}\chi_{\delta}|g|\chi_{\kappa}\chi_{\nu}\rangle \right)$$

$$\gamma_{\delta,\kappa} = \sum_{i,\,occupied} C_{\delta,i} C_{\kappa,i} \;,\;\; \gamma_{\delta,\kappa}^{ex} = \sum_{i,\,occ\,and\,same\,spin} C_{\delta,i} C_{\kappa,i} \;,\;\; g = \frac{1}{|r - r'|}$$

Note: only occupied basis functions in the Fock operator. The Fock matrix is then substituted back into the first equation and coefficients are recalculated. The procedure is carried out until a self-consistent minimum energy is found. The resulting self-consistent field (SCF) energy is the Hartree-Fock procedure.

# The Density Matrix

# The Density Matrix

We have discussed the general idea that each electron experiences the combined electrostatic potential of all of the other electrons. The density matrix is the way that the potential is calculated from the coefficients of the molecular orbitals. Thus, the density matrix is the starting point for the variational procedure. The charge density is equal to the sum of the squares of the occupied molecular orbitals:

$$\rho(r) = 2 \sum_c^{N/2} \psi_c^*(r)\,\psi_c(r_2) \;=\; 2 \sum_c^{N/2} \sum_\nu c_{\nu c}^* \phi_c^*(r) \sum_\mu c_{\mu c} \phi_c(r)$$

$$= \sum_{\mu\nu} \left[ 2 \sum_c^{N/2} c_{\nu c}^* c_{\mu c} \right] \phi_c^*(r)\phi_c(r) \;=\; \sum_{\mu\nu} P_{\mu\nu}\, \phi_c^*(r)\phi_c(r)$$

# The Density Matrix

These equations define the density matrix as:

$$P_{\mu\nu} = 2 \sum_c^{N/2} c_{vc}^* c_{\mu c}$$

Using this definition we can rewrite the closed shell Fock operator to include the density matrix. This shows how the mean-field potential enters into the calculation.

$$f(r_1) = h(r_1)$$

$$+ \sum_{\lambda\sigma} P_{\lambda\sigma} \left( \int dr_2 \, \phi_\lambda^*(r_2) r_{12}^{-1} \phi_\lambda(r_2) - \frac{1}{2} \int dr_2 \, \phi_\lambda^*(r_2) r_{12}^{-1} \phi_\sigma(r_1) \right)$$

# The Density Matrix

Using the Fock operator we can obtain the Fock matrix

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{c}^{N/2}\sum_{\lambda\sigma} c_{\lambda c}^{*}c_{\sigma c}\left(2(\mu\nu|\lambda\sigma) - (\mu\lambda|\sigma\nu)\right)$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda\sigma} P_{\lambda\sigma}\left((\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right)$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} + G_{\mu\nu}$$

The core hamiltonian $H_{\mu\nu}^{core}$ is a one-electron hamiltonian that only needs to be evaluated once in the procedure. The $G_{\mu\nu}$ matrix is a two-electron matrix that changes on each iteration.

# The self-consistent field method

The effective or average potential can be used in a one electron hamiltonian operator for electron 1

$$\hat{H}_1^{eff}(r_1) = -\frac{1}{2}\nabla_1^2 - \frac{2}{r} + V_1^{eff}(r_1)$$

The Schrödinger equation is solved for electron 1

$$\hat{H}_1^{eff}\phi(r_1) = \varepsilon_1\phi(r_1)$$

Start with a trial function $\phi(r_2)$ and solve for $\phi(r_1)$. Using $\phi(r_1)$ calculate an effective potential for 2 and solve for $\phi(r_2)$. Continue until convergence is reached.

# The self-consistent field method

The HF procedure is an iterative computation of the variational coefficients, which are the coefficients of the molecular orbitals. The iterations proceed until the change in the energy on each step is less than a convergence criterion. A typical criterion is less than $10^{-6}$ Hartrees (< 0.0026 kJ/mol). The concept of a self-consistent field (SCF) emerges from the fact that the Fock equations have reduced the many electron problem to a one-electron problem. The potential for each electron arises from the mean potential of all of the other electrons. The solution must be self-consistent in terms of the potential on each electron. As the potentials become more consistent the energy decreases according to the variational principle. That is why the change in the energy is the convergence criterion for the SCF calculation.

# Self-Consistent Field Procedure

We outline the mathematical steps in the procedure in the following:
1. Specify a molecules with coordinates {R}, atomic charges {Z}, number of electrons {N} and a basis set {$\phi$}.
2. Based on an initial guess for the coefficients calculate $S_{\mu\nu}$ and the two-electron integrals $J_{\mu\nu}$ and $K_{\mu\nu}$.
3. Diagonalize the overlap matrix **S**, i.e. $\mathbf{X^T S X} = \mathbf{I}$
4. Calculate the density matrix **P**
5. Calculate the matrix **G** from the density matrix and the two-electron integrals.
6. Add **G** to the Hamiltonian to obtain the Fock matrix, $\mathbf{F} = \mathbf{H^{core}} + \mathbf{G}$.
7. Calculate the transformed Fock matrix $\mathbf{F'} = \mathbf{X^T F X}$.
8. Diagonalize **F'** to obtain **C'** and $\varepsilon$.
9. Calculate $\mathbf{C} = \mathbf{X C'}$.
10. Form a new density matrix **P** from **C**.
11. Check for convergence. If the procedure has not converged, return to step 5 with the new density matrix.
12. If the procedure has converged then proceed to calculate molecular orbitals and any requested molecular properties.

# Summary of methods

1. Determine the optimum atomic orbitals. This is done by a variational procedure for each atom using the exponent $\zeta$ as the parameter. More than one STO can be used per atomic orbital (e.g. double-zeta basis). The GTO requires parameterization of multiple Gaussian functions per STO.
2. Form linear combinations of the atomic orbitals at the positions indicated by a molecular geometry.  Note that this is initially just a guess and the set of coefficients, which gives The lowest energy must be calculated in a number of tries (cycles) of the HF procedure. The HF procedure involves Solution of the **HC** – **ESC** = 0 matrix equations.
3. Perform the HF procedure repeatedly until a self-consistent solution of the equations for the coefficients is obtained.  This is the self-consistent field (SCF) method.