Basis Functions and Integrals

Review

- Defined our electronic Hamiltonian

$$\hat{H} = -\sum_i \frac{1}{2}\nabla^2_{\boldsymbol{r}_i} - \sum_i \sum_A \frac{Z_A}{|\boldsymbol{R}_A - \boldsymbol{r}_i|} + \sum_{i<j} \frac{1}{\boldsymbol{r}_{ij}} + V_{\text{nuc}}$$

$$\hat{H} = \sum_i \hat{h}(i) + \sum_{i<j} \hat{g}(i,j) + V_{\text{nuc}}$$

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- Selected a general form for an N-electron wavefunction: an *antisymmetric product* of one electron wavefunctions (spin orbitals), a Slater determinant

$$\Phi = \sqrt{N!}\hat{A}(\psi_1^1 \psi_2^2 \ldots \psi_N^N)$$

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- Selected a general form for an N-electron wavefunction: an *antisymmetric product* of one electron wavefunctions (spin orbitals), a Slater determinant

$$\Phi = \sqrt{N!}\hat{A}(\psi_1^1 \psi_2^2 \dots \psi_N^N)$$

- Solved for the expectation value of our electronic energy when the wavefunction is a normalized Slater determinant composed of orthonormal spin orbitals

$$E = \langle \Phi | \hat{H} | \Phi \rangle = \sum_i \langle \psi_i^i | \hat{h}(i) | \psi_i^i \rangle + \sum_{i<j} \langle \psi_i^i \psi_j^j | \hat{g}(i,j) | \psi_i^i \psi_j^j \rangle - \langle \psi_i^i \psi_j^j | \hat{g}(i,j) | \psi_j^i \psi_i^j \rangle$$

Review

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- Integrated out spin functions to arrive at the energy expression for the special case of a **closed-shell** system, in terms of just **spatial orbitals**

$$E = 2 \sum_i^{N/2} \langle \phi_i | \hat{h}(i) | \phi_i \rangle + \sum_i^{N/2} \sum_j^{N/2} 2 \langle \phi_i \phi_j | \hat{g}(i,j) | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g}(i,j) | \phi_j \phi_i \rangle$$

- How to find a good set of ϕ_i ?

Review

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$$E = 2\sum_{i}^{N/2}\langle\phi_i|\hat{h}(i)|\phi_i\rangle + \sum_{i}^{N/2}\sum_{j}^{N/2} 2\langle\phi_i\phi_j|\hat{g}(i,j)|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\hat{g}(i,j)|\phi_j\phi_i\rangle$$

- How to find a good set of ϕ_i ?

Minimizing the **energy** under the **constraint** that the spin orbitals remain **orthonormal** gives us the **Hartree-Fock equations**, which describe the conditions the *best possible* spin orbitals satisfy. These *best possible* spin orbitals give the *best possible* single Slater determinant wavefunction and *best possible* energy

$$\hat{f}\,\phi_i = \epsilon_i\phi_i$$

- Solving these equations for a given molecular system is extremely difficult

Review

$$\hat{f}\,\phi_i = \epsilon_i \phi_i$$

- Expanding these molecular orbitals in a basis of fixed functions (atomic orbitals) simplifies things: $$\phi_i = \sum_q \chi_q C_{qi}$$

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- Expanding these molecular orbitals in a basis of fixed functions (atomic orbitals) simplifies things: $$\phi_i = \sum_q \chi_q C_{qi}$$

- Roothaan-Hall Equations $$\boldsymbol{FC} = \boldsymbol{SC\epsilon}$$

$$\langle \chi_p \mid \hat{f} \mid \chi_q \rangle = \langle \chi_p \mid \hat{h} \mid \chi_q \rangle + \sum_r^m \sum_s^m D_{rs} \left[2\langle \chi_p \chi_r \mid \hat{g} \mid \chi_q \chi_s \rangle - \langle \chi_p \chi_r \mid \hat{g} \mid \chi_s \chi_q \rangle \right]$$

$$E = 2\sum_{pq} D_{pq} \langle \chi_p \mid \hat{h} \mid \chi_q \rangle + \sum_{pqrs} D_{pq} D_{rs} [2\langle \chi_p \chi_r \mid \hat{g} \mid \chi_q \chi_s \rangle - \langle \chi_p \chi_r \mid \hat{g} \mid \chi_s \chi_q \rangle]$$

- We have so far said nothing about what the AO functions χ_p are

$$\langle \chi_p \mid \hat{f} \mid \chi_q \rangle = \langle \chi_p \mid \hat{h} \mid \chi_q \rangle + \sum_r^m \sum_s^m D_{rs} \left[2\langle \chi_p \chi_r \mid \hat{g} \mid \chi_q \chi_s \rangle - \langle \chi_p \chi_r \mid \hat{g} \mid \chi_s \chi_q \rangle \right]$$

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- What are these AO functions?
- How do we evaluate these integrals?

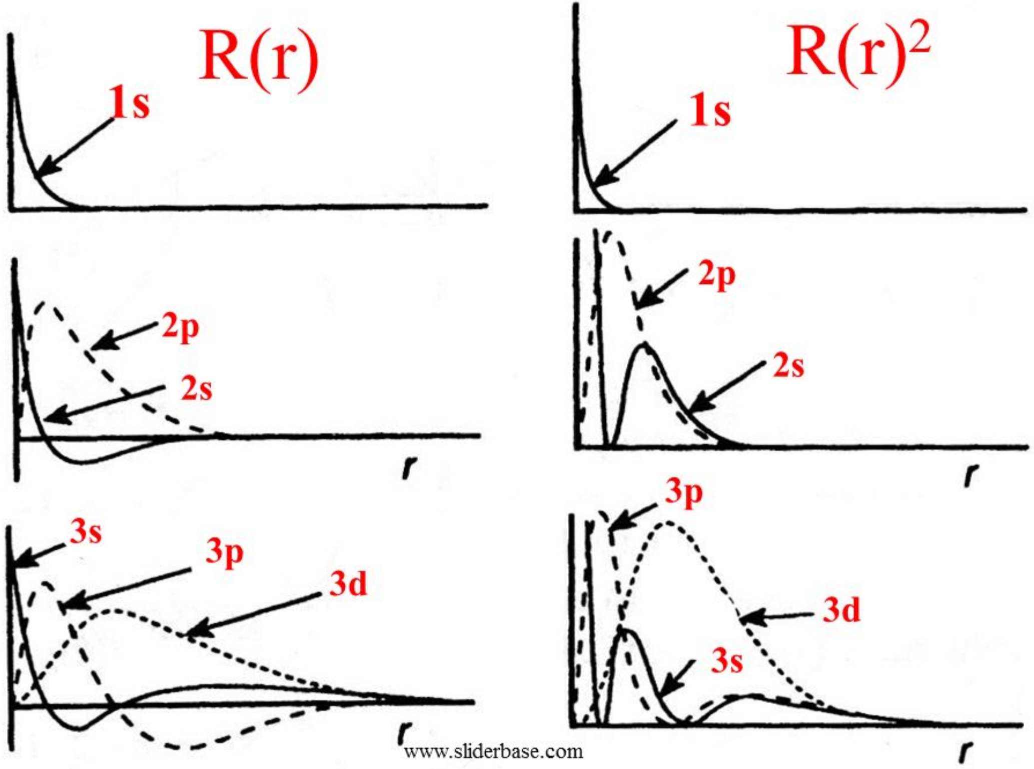
What makes a good AO basis function?

- One and two-integrals consisting of these AO’s must not diverge, and they must be evaluable

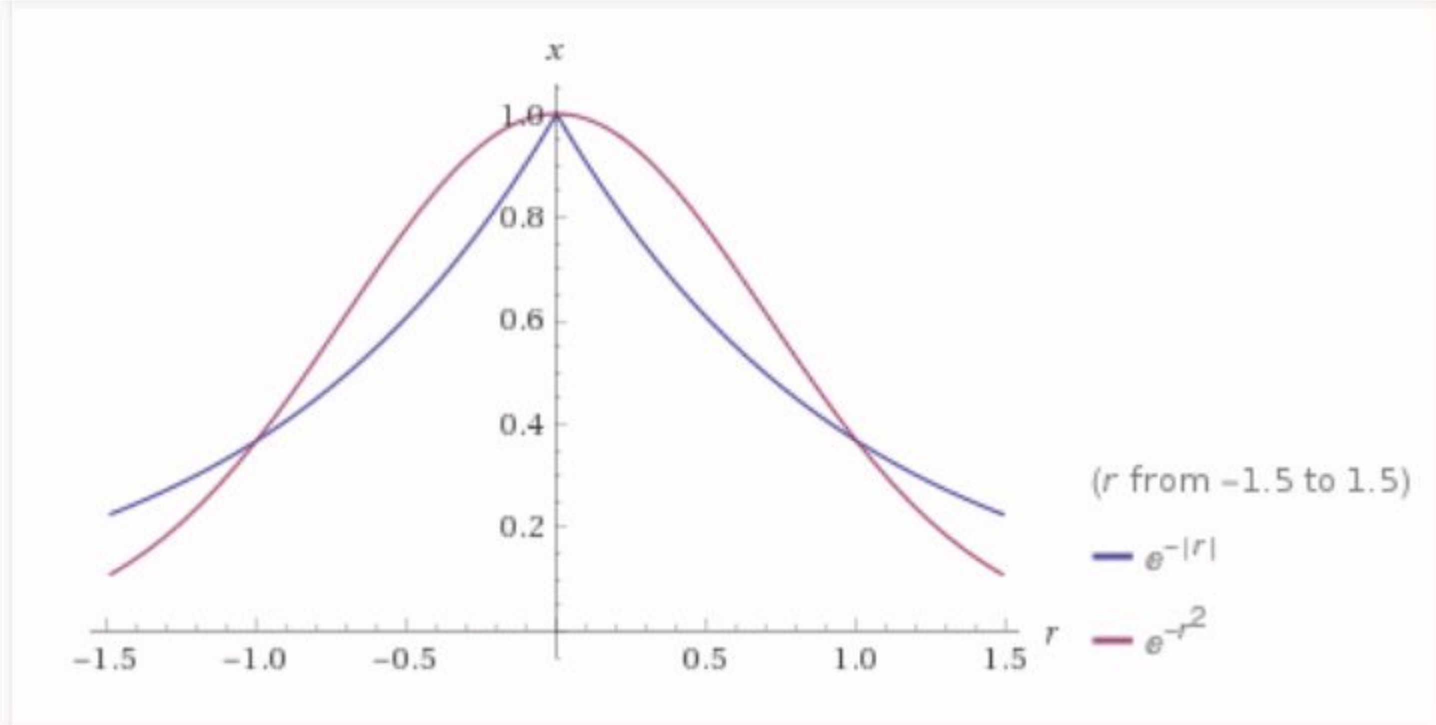
- The AO basis functions should be similar to known one-electron wavefunctions

- The AO basis functions should be systematically improvable, and allow one to approach ‘completeness’ with respect to the space of all one-electron square integrable functions

Hydrogen Atom Radial Wavefunctions



Slater and Gaussian Functions



- Two electron integrals over Slater functions: very expensive
- Two electron integrals over Gaussian functions: very cheap
- Linear combinations of Gaussians (*contracted* Gaussians) mimic Slater/Hydrogen-like wavefunctions

http://fooplot.com/#W3sidHlwZSI6MCwiZXEiOiIwLjEzMCooMiowLjA2NTEvcGkpXigzLzQpKmV4cCgtMC4wNjUxKnheMikrMC40MTYqKDIqMC4xNTgvcGkpXigzLzQpKmV4cCgtMC4xNTgqeF4yKSswLjM3MSooMiowLjQwNy9waSleKDMvNCkqZXhwKC0wLjQwNyp4XjIpKzAuMTY5KigyKjEuMTkvcGkpXigzLzQpKmV4cCgtMS4xOSp4XjIpKzAuMDQ5NCooMio0LjI0L3BpKV4oMy80KSpleHAoLTQuMjQqeF4yKSswLjAwOTE2KigyKjIzLjEvcGkpXigzLzQpKmV4cCgtMjMuMSp4XjIpIiwiY29sb3IiOiIjRUIxM0YyIn0seyJ0eXBlIjowLCJlcSI6IjAuMjkyKigyKjAuMDg4L3BpKV4oMy80KSpleHAoLTAuMDg4KnheMikrMC41MzMqKDIqMC4yNjUvcGkpXigzLzQpKmV4cCgtMC4yNjUqeF4yKSswLjI2MCooMiowLjk1NS9waSleKDMvNCkqZXhwKC0wLjk1NSp4XjIpKzAuMDU2OCooMio1LjIyL3BpKV4oMy80KSpleHAoLTUuMjIqeF4yKSIsImNvbG9yIjoiIzBBQ0VGNSJ9LHsidHlwZSI6MCwiZXEiOiIwLjY3OSooMiowLjE1Mi9waSleKDMvNCkqZXhwKC0wLjE1Mip4XjIpKzAuNDMwKigyKjAuODUyL3BpKV4oMy80KSpleHAoLTAuODUyKnheMikiLCJjb2xvciI6IiNGQTAzMDMifSx7InR5cGUiOjAsImVxIjoiKDEvcGkpXigxLzIpKmV4cCgtYWJzKHgpKSIsImNvbG9yIjoiIzAwMDAwMCJ9LHsidHlwZSI6MTAwMCwid2luZG93IjpbIi01IiwiNSIsIjAiLCIwLjYiXX1d

Gaussian Basis Functions

"**Primitive**" Gaussian basis function:

$$\chi_k(\boldsymbol{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z}\exp[-\alpha_k(\boldsymbol{r} - \boldsymbol{A})^2]$$

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$$\chi_k(\boldsymbol{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z} \exp[-\alpha_k(\boldsymbol{r} - \mathbf{A})^2]$$

- $\boldsymbol{a} = (a_x, a_y, a_z)$ is the *angular momentum*, or *quantum numbers* of the Gaussian. The sum of this vector is the *total angular momentum*
- We label the Gaussians according to their angular momentum vector
  - *s*-type Gaussian: $(a_x, a_y, a_z) = (0, 0, 0)$

$$p_x \implies \boldsymbol{a} = (1, 0, 0)$$

$$p_y \implies \boldsymbol{a} = (0, 1, 0)$$

$$p_z \implies \boldsymbol{a} = (0, 0, 1)$$

$$d_{xy} \implies \boldsymbol{a} = (1, 1, 0)$$

$$f_{xyz} \implies \boldsymbol{a} = (1, 1, 1)$$

$$g_{xxxx} \implies \boldsymbol{a} = (4, 0, 0)$$

Contracted Gaussians

$$\chi_k(\boldsymbol{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z} \exp[-\alpha_k(\boldsymbol{r} - \boldsymbol{A})^2]$$

Contracted Gaussian: Linear combination of *primitive* Gaussians

$$\chi^c = \sum_k^K D_k \chi_k$$

```
#----------------------------------------------------------------------
# Basis Set Exchange
# Version v0.8.11
# https://www.basissetexchange.org
#----------------------------------------------------------------------
#   Basis set: STO-3G
# Description: STO-3G Minimal Basis (3 functions/AO)
#        Role: orbital
#     Version: 1  (Data from Gaussian09)
#----------------------------------------------------------------------


BASIS "ao basis" PRINT
#BASIS SET: (6s,3p) -> [2s,1p]
O    S
      0.1307093214E+03       0.1543289673E+00
      0.2380886605E+02       0.5353281423E+00
      0.6443608313E+01       0.4446345422E+00
O    S
      0.5033151319E+01      -0.9996722919E-01
      0.1169596125E+01       0.3995128261E+00
      0.3803889600E+00       0.7001154689E+00
O    P
      0.5033151319E+01       0.1559162750E+00
      0.1169596125E+01       0.6076837186E+00
      0.3803889600E+00       0.3919573931E+00
END
```

Quick Note: Spherical vs Cartesian Gaussians

- Higher angular momentum Gaussians in terms of Cartesian coordinates can be transformed into a set of spherical functions.

$$d_{xx}\,, d_{xy}\,, d_{xz}\,, d_{yy}\,, d_{yz}\,, d_{zz} \;\rightarrow\; d_{x^2-y^2}\,, d_{xy}\,, d_{xz}\,, d_{yz}\,, d_{3z^2-r^2}$$

- 6 *d* → 5 *d*
- 10 *f* → 7 *f*
- 15 *g* → 9 *g*

Does not change relative energies, but it changes absolute energies significantly!

Integrals over Gaussian Functions

For Hartree-Fock and post-Hartree-Fock methods, we need to evaluate:

- Overlap integrals
- Electron-kinetic energy integrals
- Nuclear-electron potential energy integrals
- Electron-repulsion integrals

$$\boldsymbol{FC} = \boldsymbol{SC\epsilon}$$

$$\langle \chi_p \mid \hat{f} \mid \chi_q \rangle = \langle \chi_p \mid \hat{h} \mid \chi_q \rangle + \sum_r^m \sum_s^m D_{rs} \left[2\langle \chi_p \chi_r \mid \hat{g} \mid \chi_q \chi_s \rangle - \langle \chi_p \chi_r \mid \hat{g} \mid \chi_s \chi_q \rangle \right]$$

Electronic wave functions

I. A general method of calculation for the stationary states of any molecular system

By S. F. Boys, *Theoretical Chemistry Department, University of Cambridge**

(*Communicated by Sir Alfred Egerton, F.R.S.—Received* 31 *August* 1949)

This communication deals with the general theory of obtaining numerical electronic wave functions for the stationary states of atoms and molecules. It is shown that by taking Gaussian functions, and functions derived from these by differentiation with respect to the parameters, complete systems of functions can be constructed appropriate to any molecular problem, and that all the necessary integrals can be explicitly evaluated. These can be used in connexion with the molecular orbital method, or localized bond method, or the general method of treating linear combinations of many Slater determinants by the variational procedure. This general method of obtaining a sequence of solutions converging to the accurate solution is examined. It is shown that the only obstacle to the evaluation of wave functions of any required degree of accuracy is the labour of computation. A modification of the general method applicable to atoms is discussed and considered to be extremely practicable.

Integrals over *s*-type Gaussian functions

Notation:

$$\boldsymbol{a} := \chi_a(\boldsymbol{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z} \exp[-\alpha_a(\boldsymbol{r} - \boldsymbol{A})^2]$$

$$\boldsymbol{b} := \chi_b(\boldsymbol{r}) = (x - B_x)^{b_x}(y - B_y)^{b_y}(z - B_z)^{b_z} \exp[-\alpha_b(\boldsymbol{r} - \boldsymbol{B})^2]$$

$$(\boldsymbol{a} \mid \hat{O} \mid \boldsymbol{b}) = \int \chi_a^*(\boldsymbol{r}_1)\hat{O}\chi_b(\boldsymbol{r}_1)d\boldsymbol{r}_1$$

$$(\boldsymbol{ab} \mid \boldsymbol{cd}) = \int \chi_a^*(\boldsymbol{r}_1)\chi_b(\boldsymbol{r}_1)r_{12}^{-1}\chi_c^*(\boldsymbol{r}_2)\chi_d(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

Overlap integral of two *s*-Gaussians

$$(\boldsymbol{a} \mid \boldsymbol{b}) = (s \mid s) = N_a N_b \frac{\pi}{\alpha_a + \alpha_b} \exp\left(\frac{-\alpha_a \alpha_b (\boldsymbol{A} - \boldsymbol{B})^2}{\alpha_a + \alpha_b} \right)$$

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$$N_a = \frac{\left(\frac{2\alpha_a}{\pi}\right)^{3/4} (4\alpha_a)^{(a_x+a_y+a_z)/2}}{\sqrt{(2a_x - 1)!!(2a_y - 1)!!(2a_z - 1)!!}} = \left(\frac{2\alpha_a}{\pi}\right)^{3/4}$$

Kinetic integral of two *s*-Gaussians

$$(\boldsymbol{a} \mid \hat{T} \mid \boldsymbol{b}) = (s \mid \hat{T} \mid s) = (s \mid s) \cdot (3\omega + 2\omega^2 \cdot -(\boldsymbol{A} - \boldsymbol{B})^2)$$

$$\omega = \frac{\alpha_a \alpha_b}{\alpha_a + \alpha_b}$$

Potential integral of two *s*-Gaussians

- Every potential integral depends on the entire set of nuclear coordinates in the molecule $\boldsymbol{G}_i$ and the nuclear charges Z_i

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$$\boldsymbol{P} = \frac{\alpha_a \boldsymbol{A} + \alpha_b \boldsymbol{B}}{\alpha_a + \alpha_b}$$

$$x_i = (\alpha_a + \alpha_b)(\boldsymbol{P} - \boldsymbol{G}_i)^2$$

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$$(\boldsymbol{a} \mid \hat{V} \mid \boldsymbol{b}) = (s \mid \hat{V} \mid s) = N_a N_b \frac{2\pi}{\alpha_a + \alpha_b} \exp[(\boldsymbol{A} - \boldsymbol{B})^2 \cdot -\omega] \sum_i^n -Z_i F_0(x_i)$$

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$$F_\nu(x) = \int_0^1 t^{2\nu} \exp(-xt^2) dt = \frac{1}{2x^{\nu + \frac{1}{2}}} \cdot \gamma(\nu + \frac{1}{2}, x) \cdot \Gamma(\nu + \frac{1}{2})$$

Potential integral of two *s*-Gaussians

$$\boldsymbol{P} = \frac{\alpha_a \boldsymbol{A} + \alpha_b \boldsymbol{B}}{\alpha_a + \alpha_b}$$

$$x_i = (\alpha_a + \alpha_b)(\boldsymbol{P} - \boldsymbol{G}_i)^2$$

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$$F_0(x) = \operatorname{erf}(\sqrt{x}) \frac{\sqrt{\pi}}{2\sqrt{x}}$$

ERIs (ss|ss)

$$\boldsymbol{P} = \frac{\alpha_a \boldsymbol{A} + \alpha_b \boldsymbol{B}}{\alpha_a + \alpha_b}$$

$$\boldsymbol{Q} = \frac{\alpha_c \boldsymbol{C} + \alpha_d \boldsymbol{D}}{\alpha_c + \alpha_d}$$

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$$T = \frac{(\alpha_a + \alpha_b)(\alpha_c + \alpha_d)}{\alpha_a + \alpha_b + \alpha_c + \alpha_d}(\boldsymbol{P} - \boldsymbol{Q})^2$$

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$$K_{AB} = 2^{1/2}\frac{\pi^{5/4}}{\alpha_a + \alpha_b}\exp\left[-\frac{\alpha_a\alpha_b}{\alpha_a + \alpha_b}(\boldsymbol{A} - \boldsymbol{B})^2\right]$$

$$K_{CD} = 2^{1/2}\frac{\pi^{5/4}}{\alpha_c + \alpha_d}\exp\left[-\frac{\alpha_c\alpha_d}{\alpha_c + \alpha_d}(\boldsymbol{C} - \boldsymbol{D})^2\right]$$

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$$(\boldsymbol{ab} \mid \boldsymbol{cd}) = (ss \mid ss) = N_a N_b N_c N_d (\alpha_a + \alpha_b + \alpha_c + \alpha_d)^{-1/2} K_{AB} K_{CD} F_0(T)$$

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$$(\boldsymbol{ab} \mid \boldsymbol{cd}) = (ss \mid ss) = N_a N_b N_c N_d (\alpha_a + \alpha_b + \alpha_c + \alpha_d)^{-1/2} K_{AB} K_{CD} F_0(T)$$

$$F_0(x) = \mathrm{erf}(\sqrt{x}) \frac{\sqrt{\pi}}{2\sqrt{x}}$$

Easy integrals, easy life

Integrals over *s* functions are not that bad!

Integrals over higher angular momentum (*p, d, f, g…)* can be constructed from linear combinations of *s*-function integrals! (Recursion relations)

$$\frac{\partial}{\partial A_i}(\boldsymbol{a}) = 2\alpha_a(\boldsymbol{a} + \mathbf{1}_i) - a_i(\boldsymbol{a} - \mathbf{1}_i)$$

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$$\frac{\partial}{\partial A_i}(\boldsymbol{a} \mid \boldsymbol{b}) = 2\alpha_a((\boldsymbol{a} + \mathbf{1}_i) \mid \boldsymbol{b}) - a_i((\boldsymbol{a} - \mathbf{1}_i) \mid \boldsymbol{b})$$

$$\frac{\partial}{\partial A_i}(\boldsymbol{ab} \mid \boldsymbol{cd}) = 2\alpha_a((\boldsymbol{a} + \mathbf{1}_i)\boldsymbol{b} \mid \boldsymbol{cd}) - a_i((\boldsymbol{a} - \mathbf{1}_i)\boldsymbol{b} \mid \boldsymbol{cd})$$

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$$\frac{\partial}{\partial A_i}(\boldsymbol{ab} \mid \boldsymbol{cd}) = 2\alpha_a((\boldsymbol{a} + \mathbf{1}_i)\boldsymbol{b} \mid \boldsymbol{cd}) - a_i((\boldsymbol{a} - \mathbf{1}_i)\boldsymbol{b} \mid \boldsymbol{cd})$$

$$\downarrow$$

$$((\boldsymbol{a} + \mathbf{1}_i) \mid \boldsymbol{b}) = \frac{1}{2\alpha_a}\left(\frac{\partial}{\partial A_i}(\boldsymbol{a} \mid \boldsymbol{b}) + a_i((\boldsymbol{a} - \mathbf{1}_i) \mid \boldsymbol{b})\right)$$

$$((\boldsymbol{a} + \mathbf{1}_i)\boldsymbol{b} \mid \boldsymbol{cd}) = \frac{1}{2\alpha_a}\left(\frac{\partial}{\partial A_i}(\boldsymbol{ab} \mid \boldsymbol{cd}) + a_i((\boldsymbol{a} - \mathbf{1}_i)\boldsymbol{b} \mid \boldsymbol{cd})\right)$$

Overlap Recurrence Relation

$$((\boldsymbol{a} + \mathbf{1}_i) \mid \boldsymbol{b}) = (P_i - \mathrm{A}_i)(\boldsymbol{a} \mid \boldsymbol{b}) + \frac{1}{2\alpha_a} a_i((\boldsymbol{a} - \mathbf{1}_i) \mid \boldsymbol{b}) + \frac{1}{2\alpha_a} b_i(\boldsymbol{a} \mid (\boldsymbol{b} - \mathbf{1}_i))$$

$$\boldsymbol{P} = \frac{\alpha_a \boldsymbol{A} + \alpha_b \boldsymbol{B}}{\alpha_a + \alpha_b}$$

ERI Recursion

$$
\begin{aligned}
((\mathbf{a}+\mathbf{1}_i)\mathbf{b} \mid \mathbf{cd})^{(m)} &= (P_i - A_i)(\mathbf{ab} \mid \mathbf{cd})^{(m)} + (W_i - P_i)(\mathbf{ab} \mid \mathbf{cd})^{(m+1)} \\
&+ \frac{a_i}{\alpha_a}\left[((\mathbf{a}-\mathbf{1}_i)\mathbf{b} \mid \mathbf{cd})^{(m)} - \frac{\eta}{\eta+\zeta}((\mathbf{a}-\mathbf{1}_i)\mathbf{b} \mid \mathbf{cd})^{(m+1)}\right] \\
&+ \frac{b_i}{\alpha_a}\left[(\mathbf{a}(\mathbf{b}-\mathbf{1}_i) \mid \mathbf{cd})^{(m)} - \frac{\eta}{\eta+\zeta}(\mathbf{a}(\mathbf{b}-\mathbf{1}_i) \mid \mathbf{cd})^{(m+1)}\right] \\
&+ \frac{c_i}{2(\zeta+\eta)}(\mathbf{ab} \mid (\mathbf{c}-\mathbf{1}_i)\mathbf{d})^{(m+1)} + \frac{d_i}{2(\zeta+\eta)}(\mathbf{ab} \mid \mathbf{c}(\mathbf{d}-\mathbf{1}_i))^{(m+1)}
\end{aligned}
$$

$$\boldsymbol{P} = \frac{\alpha_a \boldsymbol{A} + \alpha_b \boldsymbol{B}}{\alpha_a + \alpha_b}$$

$$\boldsymbol{Q} = \frac{\alpha_c \boldsymbol{C} + \alpha_d \boldsymbol{D}}{\alpha_c + \alpha_d}$$

$$\zeta = \alpha_a + \alpha_b$$
$$\eta = \alpha_c + \alpha_d$$

$$\boldsymbol{W} = \frac{\zeta P_i + \eta Q_i}{\zeta + \eta}$$

- Wednesday:
    - Next programming project: RHF with integrals from scratch.
    - Review for Quiz
- Friday: Quiz