

# The SCF Workshop Notes 2

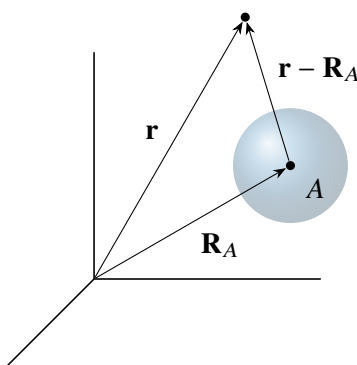
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## 2.1. How to Gaussian Integrate

Let's take a quick step back and ask the very same question that dawned on me when learning about this stuff "What is the actual mathematical form of the thing we're solving? I mean TF do I actually put into a code to compute this stuff". Let's first refamiliarize ourselves with Gaussian basis sets, and then derive our expressions using Gaussian orbitals.

In molecular calculations, you generally use a fixed molecular coordinate system, so that the basis functions are centered at position vectors  $\mathbf{R}_A$ . The value at a position vector  $\mathbf{r}$ , of a function centered at  $\mathbf{R}_A$  will depend on  $\mathbf{r} - \mathbf{R}_A$ , thus we write a general basis function as  $\phi_\mu(\mathbf{r} - \mathbf{R}_A)$  to denote that it is centered at  $\mathbf{R}_A$



**Figure 1.** Coordinate system representation for the atom centered Gaussian

Our typical unnormalized Gaussian friend looks like

$$\tilde{g}_{1s}(\mathbf{r} - \mathbf{R}_A) = e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2} \quad (2.1)$$

The normalized *1s Gaussian-type function*, centered at  $\mathbf{R}_A$ , can be written as

$$\phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_A) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2} \quad (2.2)$$

The integrals take the generic form

$$(\mu_A \nu_B | \lambda_C \sigma_D) = \int \phi_\mu^{A*}(\mathbf{r}_1) \phi_\nu^B(\mathbf{r}_1) r_{12}^{-1} \phi_\lambda^{C*}(\mathbf{r}_2) \phi_\sigma^D(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.3)$$

which will involve taking the product of Gaussian functions, fortunately this product is just another Gaussian centered at the midpoint between the two other centers

$$\phi_{1s}^{\text{GS}}(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_{1s}^{\text{GS}}(\beta, \mathbf{r} - \mathbf{R}_B) = K_{AB} \phi_{1s}^{\text{GS}}(p, \mathbf{r} - \mathbf{R}_p) \quad (2.4)$$

where this constant  $K_{AB}$  is

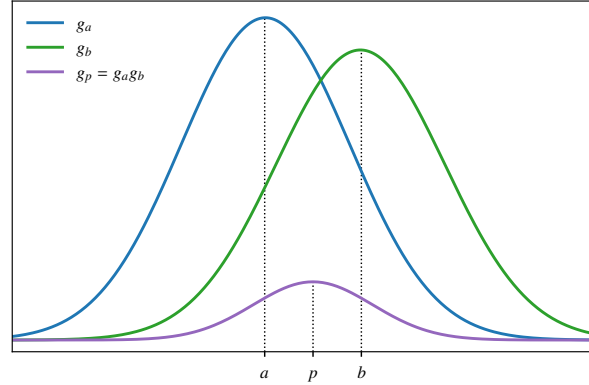
$$K_{AB} = \left(\frac{2\alpha\beta}{(\alpha + \beta)\pi}\right)^{3/4} \exp\left(-\frac{\alpha\beta}{\alpha + \beta}\right) \exp\left(-|\mathbf{R}_A - \mathbf{R}_B|^2\right) \quad (2.5)$$

The new exponent of the Gaussian centered at  $\mathbf{R}_P$  is

$$p = \alpha + \beta \quad (2.6)$$

and the third center  $P$  is on a line joining the centers  $A$  and  $B$

$$\mathbf{R}_P = (\alpha\mathbf{R}_A + \beta\mathbf{R}_B)/(\alpha + \beta) \quad (2.7)$$



**Figure 2.** Product of two Gaussian

$$(\mu_A \nu_B | \lambda_C \sigma_D) = K_{AB} K_{CD} \int \phi_{1s}^{\text{GS}}(p, \mathbf{r}_1 - \mathbf{R}_p) r_{12}^{-1} \phi_{1s}^{\text{GS}}(q, \mathbf{r}_2 - \mathbf{R}_Q) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.8)$$

The formula for a series of Gaussian, known as contracted GFs is

$$\phi_{\mu}^{\text{CGF}}(\mathbf{r} - \mathbf{R}_A) = \sum_{p=1}^L d_{p\mu} \phi_p^{\text{GF}}(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A) \quad (2.9)$$

where  $d_{p\mu}$  are the contraction coefficients

### 2.1.1 Integral Forms of 1s Gaussians

The  $\mathbf{S}$  overlap matrix has the basic form that when integrated gives us the following equation

$$\begin{aligned} S = (A|B) &= \int \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_A) \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_B) d\mathbf{r}_1 \\ &= \left( \frac{\pi}{(\alpha + \beta)} \right)^{3/2} \exp\left( -\frac{\alpha\beta}{(\alpha + \beta)} |\mathbf{R}_A - \mathbf{R}_B|^2 \right) \end{aligned}$$

Kinetic energy integral will give us this expression

$$\begin{aligned} \left( A \left| -\frac{1}{2} \nabla^2 \right| B \right) &= \int \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_A) \left( -\frac{1}{2} \nabla^2 \right) \tilde{g}_{1s}(\mathbf{r}_1 - \mathbf{R}_B) d\mathbf{r}_1 \\ &= \frac{\alpha\beta}{(\alpha + \beta)} \left[ 3 - \frac{2\alpha\beta}{(\alpha + \beta)} |\mathbf{R}_A - \mathbf{R}_B|^2 \right] \left[ \frac{\pi}{(\alpha + \beta)} \right]^{3/2} \exp\left( -\frac{\alpha\beta}{(\alpha + \beta)} |\mathbf{R}_A - \mathbf{R}_B|^2 \right) \end{aligned}$$

For the nuclear attraction integral, I'm going to have to pull a Cukier and refer you to pg. 412–414 of S&O for the exact derivation.

During the derivation (which involves Fourier transforms!—you'll never escape them, submit to their study or perish), we end up needing to introduce the  $F_0$  function, defined as

$$F_0(t) = t^{-1/2} \int_0^{t^{1/2}} e^{-y^2} dy \quad (2.10)$$

It is related to the error function by

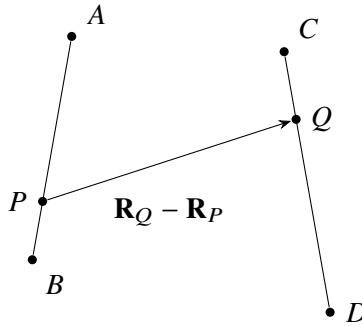
$$F_0(t) = \frac{1}{2} (\pi/t)^{1/2} \operatorname{erf}(t^{1/2}) \quad (2.11)$$

which itself is related to the Gamma function and so on, anyway, our nuclear attraction integral then becomes

$$\left( A \left| -\frac{Z_C}{r_{1C}} \right| B \right) = -\frac{2\pi}{(\alpha + \beta)} Z_C \exp\left( -\frac{\alpha\beta}{(\alpha + \beta)} |\mathbf{R}_A - \mathbf{R}_B|^2 \right) F_0\left( (\alpha + \beta) |\mathbf{R}_P - \mathbf{R}_C|^2 \right) \quad (2.12)$$

Now consider the horrid two-electron repulsion integral

$$\begin{aligned} (AB|CD) &= \exp\left( -\frac{\alpha\beta}{(\alpha + \beta)} |\mathbf{R}_A - \mathbf{R}_B|^2 - \frac{\gamma\delta}{(\gamma + \delta)} |\mathbf{R}_C - \mathbf{R}_D|^2 \right) \\ &\quad \times \int \exp(-p|\mathbf{r}_1 - \mathbf{R}_P|^2) r_{12}^{-1} \exp(-q|\mathbf{r}_2 - \mathbf{R}_Q|^2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{2\pi^{5/2}}{(\alpha + \beta)(\gamma + \delta)(\alpha + \beta + \gamma + \delta)^{1/2}} \\ &\quad \times \exp\left( -\frac{\alpha\beta}{(\alpha + \beta)} |\mathbf{R}_A - \mathbf{R}_B|^2 - \frac{\gamma\delta}{(\gamma + \delta)} |\mathbf{R}_C - \mathbf{R}_D|^2 \right) F_0\left( \frac{(\alpha + \beta)(\gamma + \delta)}{(\alpha + \beta + \gamma + \delta)} |\mathbf{R}_P - \mathbf{R}_Q|^2 \right) \end{aligned}$$



**Figure 3.** The six centers involved in the two-electron repulsion integral.