The SCF Workshop Notes 2

Lucas Aebersold May 21, 2018

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 $\mathbf{R}_A$

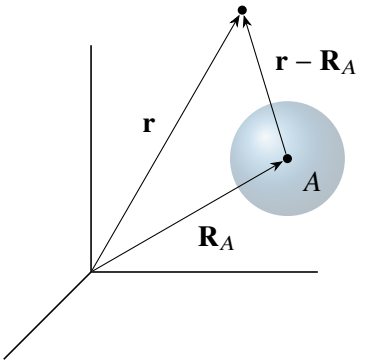

Figure 1. Coordinate system representation for the atom centered Gaussian

Our typical unnormalized Gaussian friend looks like

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

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

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

The integrals take the generic form

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

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

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

where this constant K_{AB} is

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

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

$$p = \alpha + \beta \tag{2.6}$$

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

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

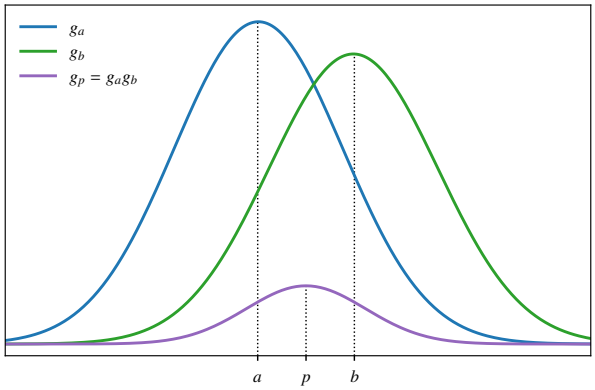

Figure 2. Product of two Gaussian

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

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

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

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

2.1.1 Integral Forms of 1s Gaussians

The **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

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

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

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

It is related to the error function by

$$F_0(t) = \frac{1}{2}(\pi/t)^{1/2}\,\mathrm{erf}(t^{1/2}) \tag{2.11}$$

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

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

Now consider the horrid two-electron repulsion integral

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

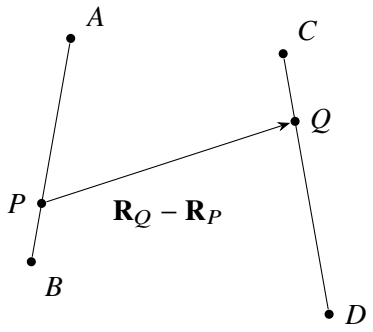

Figure 3. The six centers involved in the two-electron repulsion integral.