Notes on Coulomb overlap integrals for Gaussian orbitals

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Our goal is to compute the Coulomb overlap integral of two Gaussians centered at $\vec{p}, \vec{q} \in \mathbb{R}^3$ ($\vec{p} \neq \vec{q}$), respectively, with exponents $\alpha, \beta > 0$:

$$C^{\alpha,\beta}_{\vec{p},\vec{q}} \coloneqq \frac{(\alpha\beta)^{\frac{3}{2}}}{\pi^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathrm{e}^{-\alpha\|\vec{r}_1-\vec{p}\|^2} \, \frac{1}{\|\vec{r}_1 - \vec{r}_2\|} \, \mathrm{e}^{-\beta\|\vec{r}_2-\vec{q}\|^2} \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2. \tag{1}$$

The final result will be

$$C^{\alpha,\beta}_{\vec{p},\vec{q}} = \frac{1}{\|\vec{p}-\vec{q}\|} \operatorname{erf}\left(\sqrt{\frac{\alpha\beta}{\alpha+\beta}} \, \|\vec{p}-\vec{q}\|\right), \tag{2}$$

where $\operatorname{erf}(\cdot)$ is the error function. In the limit of delta-function like Gaussians, one obtains $\lim_{\alpha,\beta\to\infty} C^{\alpha,\beta}_{\vec{p},\vec{q}} = \frac{1}{\|\vec{p}-\vec{q}\|}$, as expected.

We will derive Eq. (2) in two ways.

Factorization of the inverse distance

To factorize the integration into Cartesian directions, we use the well-known trick of expressing $\frac{1}{r}$ (for any $r > 0$) as

$$\frac{1}{r} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \mathrm{e}^{-r^2 t^2} \, \mathrm{d}t. \tag{3}$$

Using this representation in Eq. (1) and interchanging integration orders leads to

$$C^{\alpha,\beta}_{\vec{p},\vec{q}} = \frac{(\alpha\beta)^{\frac{3}{2}}}{\pi^3} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathrm{e}^{-\alpha\|\vec{r}_1-\vec{p}\|^2} \, \mathrm{e}^{-\|\vec{r}_1-\vec{r}_2\|^2 t^2} \, \mathrm{e}^{-\beta\|\vec{r}_2-\vec{q}\|^2} \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \, \mathrm{d}t. \tag{4}$$

Note that the exponents are now quadratic functions of $\vec{r}_1$ and $\vec{r}_2$ and factorize with respect to Cartesian directions.

Due to translation and rotation symmetries, we notice that $C^{\alpha,\beta}_{\vec{p},\vec{q}}$ depends on $\vec{p}$ and $\vec{q}$ only via $\ell \coloneqq \|\vec{p}-\vec{q}\|$. Without loss of generality, we can assume that $\vec{p} = (0,0,\ell)$ and $\vec{q} = (0,0,0)$. Denoting the Cartesian coordinates of the integration variables as $\vec{r}_1 = (x_1, y_1, z_1)$ and $\vec{r}_2 = (x_2, y_2, z_2)$, respectively, we can express

$$\begin{aligned} C^{\alpha,\beta}_{\vec{p},\vec{q}} &= \frac{1}{\sqrt{\pi}} \frac{(\alpha\beta)^{\frac{3}{2}}}{\pi^3} \int_{-\infty}^{\infty} \left(\int_{\mathbb{R}} \int_{\mathbb{R}} \mathrm{e}^{-\alpha x_1^2 - (x_1-x_2)^2 t^2 - \beta x_2^2} \, \mathrm{d}x_1 \, \mathrm{d}x_2\right) \left(\int_{\mathbb{R}} \int_{\mathbb{R}} \mathrm{e}^{-\alpha y_1^2 - (y_1-y_2)^2 t^2 - \beta y_2^2} \, \mathrm{d}y_1 \, \mathrm{d}y_2\right) \\ &\qquad \times \left(\int_{\mathbb{R}} \int_{\mathbb{R}} \mathrm{e}^{-\alpha (z_1-\ell)^2 - (z_1-z_2)^2 t^2 - \beta z_2^2} \, \mathrm{d}z_1 \, \mathrm{d}z_2\right) \mathrm{d}t \\ &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \left(\frac{\alpha\beta}{\alpha\beta + t^2(\alpha+\beta)}\right)^{\frac{3}{2}} \mathrm{e}^{-\alpha\beta\ell^2 t^2 / \left(\alpha\beta + t^2(\alpha+\beta)\right)} \, \mathrm{d}t. \end{aligned} \tag{5}$$

Since the integrand is symmetric with respect to $t \to -t$, we can equivalently integrate over $[0, \infty)$ and multiply the result by 2. Next, we substitute

$$u = \frac{\alpha\beta\ell^2 t^2}{\alpha\beta + t^2(\alpha+\beta)}. \tag{6}$$

Performing the integration variable substitution results in

$$C^{\alpha,\beta}_{\vec{p},\vec{q}} = \frac{2}{\sqrt{\pi}} \int_0^{\frac{\alpha\beta}{\alpha+\beta}\ell^2} \frac{\mathrm{e}^{-u}}{2\ell\sqrt{u}} \mathrm{d}u = \frac{1}{\ell} \operatorname{erf}\left(\sqrt{\frac{\alpha\beta}{\alpha+\beta}} \, \ell\right), \tag{7}$$

which agrees with Eq. (2).

Boys' approach

The following derivation follows the historic paper by S. F. Boys [1]. We first evaluate the $\vec{r}_2$ integral:

$$I_{\vec{q}}^{\beta}(\vec{r}_1) := \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \frac{1}{\|\vec{r}_1 - \vec{r}_2\|} \, \mathrm{e}^{-\beta\|\vec{r}_2 - \vec{q}\|^2} \, \mathrm{d}^3 r_2. \tag{8}$$

Shifting the origin of the coordinate system for integration to $\vec{q}$ leads to

$$I_{\vec{q}}^{\beta}(\vec{r}_1) = \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \int_{\mathbb{R}^3} \frac{1}{\|\vec{r}_1 - \vec{q} - \vec{s}\|} \, \mathrm{e}^{-\beta\|\vec{s}\|^2} \, \mathrm{d}^3 s. \tag{9}$$

Next, we partition the integral into the ball with radius $\|\vec{r}_1 - \vec{q}\|$ and its complement:

$$I_{\vec{q}}^{\beta}(\vec{r}_1) = \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \int_{\|\vec{s}\| \le \|\vec{r}_1 - \vec{q}\|} \frac{1}{\|\vec{r}_1 - \vec{q} - \vec{s}\|} \, \mathrm{e}^{-\beta\|\vec{s}\|^2} \, \mathrm{d}^3 s + \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} \int_{\|\vec{s}\| > \|\vec{r}_1 - \vec{q}\|} \frac{1}{\|\vec{r}_1 - \vec{q} - \vec{s}\|} \, \mathrm{e}^{-\beta\|\vec{s}\|^2} \, \mathrm{d}^3 s. \tag{10}$$

The first integral on the right describes the Coulomb potential at $\vec{r}_1 - \vec{q}$ generated by a spherically symmetric charge distribution. Since the point $\vec{r}_1 - \vec{q}$ is at the boundary of this charge distribution, the distribution acts like a point charge at the origin (with the same overall charge). Expressed in spherical coordinates, we obtain

$$\begin{aligned} \int_{\|\vec{s}\| \le \|\vec{r}_1 - \vec{q}\|} \frac{1}{\|\vec{r}_1 - \vec{q} - \vec{s}\|} \, \mathrm{e}^{-\beta\|\vec{s}\|^2} \, \mathrm{d}^3 s &= \frac{1}{\|\vec{r}_1 - \vec{q}\|} \int_{\|\vec{s}\| \le \|\vec{r}_1 - \vec{q}\|} \mathrm{e}^{-\beta\|\vec{s}\|^2} \, \mathrm{d}^3 s = \frac{4\pi}{\|\vec{r}_1 - \vec{q}\|} \int_0^{\|\vec{r}_1 - \vec{q}\|} \mathrm{e}^{-\beta s^2} \, s^2 \, \mathrm{d}s \\ = \frac{4\pi}{\|\vec{r}_1 - \vec{q}\|} \left(-\frac{1}{2\beta} \, \mathrm{e}^{-\beta\|\vec{r}_1 - \vec{q}\|^2} \|\vec{r}_1 - \vec{q}\| + \frac{1}{2\beta} \int_0^{\|\vec{r}_1 - \vec{q}\|} \mathrm{e}^{-\beta s^2} \, \mathrm{d}s \right) &= -\frac{2\pi}{\beta} \, \mathrm{e}^{-\beta\|\vec{r}_1 - \vec{q}\|^2} + \frac{2\pi}{\beta\|\vec{r}_1 - \vec{q}\|} \int_0^{\|\vec{r}_1 - \vec{q}\|} \mathrm{e}^{-\beta s^2} \, \mathrm{d}s. \end{aligned} \tag{11}$$

For the third equal sign we have used integration by parts together with $\mathrm{e}^{-\beta s^2} s = \frac{\mathrm{d}}{\mathrm{d}s}(-\frac{1}{2\beta} \mathrm{e}^{-\beta s^2})$. The second integral on the right in Eq. (10) corresponds to the potential inside a hollow sphere. This potential is constant, and equal to the value at the origin. One obtains

$$\int_{\|\vec{s}\| > \|\vec{r}_1 - \vec{q}\|} \frac{1}{\|\vec{r}_1 - \vec{q} - \vec{s}\|} \, \mathrm{e}^{-\beta\|\vec{s}\|^2} \, \mathrm{d}^3 s = \int_{\|\vec{s}\| > \|\vec{r}_1 - \vec{q}\|} \frac{1}{\|\vec{s}\|} \, \mathrm{e}^{-\beta\|\vec{s}\|^2} \, \mathrm{d}^3 s = 4\pi \int_{\|\vec{r}_1 - \vec{q}\|}^{\infty} \mathrm{e}^{-\beta s^2} \, s \, \mathrm{d}s = \frac{2\pi}{\beta} \, \mathrm{e}^{-\beta\|\vec{r}_1 - \vec{q}\|^2}. \tag{12}$$

Summing Eqs. (11) and (12) leads to

$$I_{\vec{q}}^{\beta}(\vec{r}_1) = \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \frac{2}{\|\vec{r}_1 - \vec{q}\|} \int_0^{\|\vec{r}_1 - \vec{q}\|} \mathrm{e}^{-\beta s^2} \, \mathrm{d}s. \tag{13}$$

Re-inserting this result into Eq. (1) gives:

$$\begin{aligned} C_{\vec{p},\vec{q}}^{\alpha,\beta} &= \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} 2 \int_{\mathbb{R}^3} \mathrm{e}^{-\alpha\|\vec{r}_1 - \vec{p}\|^2} \frac{1}{\|\vec{r}_1 - \vec{q}\|} \int_0^{\|\vec{r}_1 - \vec{q}\|} \mathrm{e}^{-\beta s^2} \, \mathrm{d}s \, \mathrm{d}^3 r_1 \\ &= \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} 2 \int_{\mathbb{R}^3} \mathrm{e}^{-\alpha\|\vec{r} - (\vec{p} - \vec{q})\|^2} \frac{1}{\|\vec{r}\|} \int_0^{\|\vec{r}\|} \mathrm{e}^{-\beta s^2} \, \mathrm{d}s \, \mathrm{d}^3 r. \end{aligned} \tag{14}$$

We now switch to spherical coordinates (r, θ, φ) for $\vec{r}$, such that the z-axis points in the direction of $\vec{p} - \vec{q}$. The φ integral contributes 2π (since the integrand does not depend on φ). Together with the Jacobi determinant $r^2 \sin(\theta)$ due to the switch to spherical coordinates, one obtains

$$C_{\vec{p},\vec{q}}^{\alpha,\beta} = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} 4\pi \int_0^{\infty} \left(\int_0^{\pi} \mathrm{e}^{-\alpha\left(r^2 - 2\cos(\theta) r \|\vec{p} - \vec{q}\| + \|\vec{p} - \vec{q}\|^2\right)} \sin(\theta) \mathrm{d}\theta \right) r \int_0^r \mathrm{e}^{-\beta s^2} \, \mathrm{d}s \, \mathrm{d}r. \tag{15}$$

The integral with respect to θ can be evaluated directly, leading to

$$\begin{aligned} C_{\vec{p},\vec{q}}^{\alpha,\beta} &= \frac{1}{\|\vec{p} - \vec{q}\|} \frac{2\sqrt{\alpha\beta}}{\pi} \int_0^{\infty} \left(\mathrm{e}^{-\alpha\left(r^2 - 2r\|\vec{p} - \vec{q}\| + \|\vec{p} - \vec{q}\|^2\right)} - \mathrm{e}^{-\alpha\left(r^2 + 2r\|\vec{p} - \vec{q}\| + \|\vec{p} - \vec{q}\|^2\right)} \right) \int_0^r \mathrm{e}^{-\beta s^2} \, \mathrm{d}s \, \mathrm{d}r \\ &= \frac{1}{\|\vec{p} - \vec{q}\|} \frac{2\sqrt{\alpha\beta}}{\pi} \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha(r - \|\vec{p} - \vec{q}\|)^2} \int_0^r \mathrm{e}^{-\beta s^2} \, \mathrm{d}s \, \mathrm{d}r. \end{aligned} \tag{16}$$

Thus, $C^{\alpha,\beta}_{\vec{p},\vec{q}}$ depends on $\vec{p}$ and $\vec{q}$ only via $\ell \coloneqq \|\vec{p}-\vec{q}\|$.

As in Ref. [1], we now use a trick to evaluate the nested integral

$$\tilde{C}^{\alpha,\beta}(\ell) \coloneqq \frac{2\sqrt{\alpha\beta}}{\pi} \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha(r-\ell)^2} \int_0^r \mathrm{e}^{-\beta s^2}\,\mathrm{d}s\,\mathrm{d}r. \tag{17}$$

Namely, we can use integration by parts by considering its derivative with respect to ℓ:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\ell}\tilde{C}^{\alpha,\beta}(\ell) &= \frac{2\sqrt{\alpha\beta}}{\pi} \int_{-\infty}^{\infty} \left(\frac{\mathrm{d}}{\mathrm{d}\ell}\,\mathrm{e}^{-\alpha(r-\ell)^2}\right) \int_0^r \mathrm{e}^{-\beta s^2}\,\mathrm{d}s\,\mathrm{d}r = \frac{2\sqrt{\alpha\beta}}{\pi} \int_{-\infty}^{\infty} -\left(\frac{\mathrm{d}}{\mathrm{d}r}\,\mathrm{e}^{-\alpha(r-\ell)^2}\right) \int_0^r \mathrm{e}^{-\beta s^2}\,\mathrm{d}s\,\mathrm{d}r \\ &= \frac{2\sqrt{\alpha\beta}}{\pi} \int_{-\infty}^{\infty} \mathrm{e}^{-\alpha(r-\ell)^2}\,\mathrm{e}^{-\beta r^2}\,\mathrm{d}r = \frac{2}{\sqrt{\pi}} \frac{\sqrt{\alpha\beta}}{\sqrt{\alpha+\beta}}\,\mathrm{e}^{-\frac{\alpha\beta}{\alpha+\beta}\ell^2}\,.\end{aligned} \tag{18}$$

We also note that $\tilde{C}^{\alpha,\beta}(0) = 0$ due to the anti-symmetry of the integrand upon $r \to -r$ for $\ell = 0$. Integrating Eq. (18) with respect to ℓ leads to

$$\tilde{C}^{\alpha,\beta}(\ell) = \frac{2}{\sqrt{\pi}} \frac{\sqrt{\alpha\beta}}{\sqrt{\alpha+\beta}} \int_0^{\ell} \mathrm{e}^{-\frac{\alpha\beta}{\alpha+\beta}\tilde{x}^2}\,\mathrm{d}\tilde{x} = \frac{2}{\sqrt{\pi}} \int_0^{\frac{\sqrt{\alpha\beta}}{\sqrt{\alpha+\beta}}\ell} \mathrm{e}^{-x^2}\,\mathrm{d}x = \mathrm{erf}\left(\frac{\sqrt{\alpha\beta}}{\sqrt{\alpha+\beta}}\ell\right). \tag{19}$$

Inserting this relation into Eq. (16), we arrive at the final result

$$C^{\alpha,\beta}_{\vec{p},\vec{q}} = \frac{1}{\|\vec{p}-\vec{q}\|}\,\mathrm{erf}\left(\sqrt{\frac{\alpha\beta}{\alpha+\beta}}\,\|\vec{p}-\vec{q}\|\right). \tag{20}$$

[1] S. F. Boys, Electronic wave functions I. A general method of calculation for the stationary states of any molecular system, Proc. R. Soc. Lond. A **200**, 542 (1950).