APPENDIX P

Molecular Integrals with Gaussian Type Orbitals 1s

The normalized 1s spherically symmetric Gaussian Type Orbital (GTO) centered in the point shown by the vector $\boldsymbol{R}_p$ reads as

$$\chi_p \equiv \left(\frac{2\alpha_p}{\pi}\right)^{\frac{3}{4}} \exp\left(-\alpha_p |\boldsymbol{r} - \boldsymbol{R}_p|^2\right).$$

The molecular integrals usually involve at most four such orbitals: χ_p, χ_q, χ_r, χ_s, with the corresponding centers $\boldsymbol{R}_p, \boldsymbol{R}_q, \boldsymbol{R}_r, \boldsymbol{R}_s$, and the exponents $\alpha_p, \alpha_q, \alpha_r, \alpha_s$, respectively. Since any product of the 1s GTOs represents a non-normalized 1s GTO centered between the centers of the individual GTOs (see p. 426), let us denote the center of $\chi_p \chi_q$ by $\boldsymbol{R}_k = \frac{\alpha_p \boldsymbol{R}_p + \alpha_q \boldsymbol{R}_q}{\alpha_p + \alpha_q}$, and the center of $\chi_r \chi_s$ by $\boldsymbol{R}_l = \frac{\alpha_r \boldsymbol{R}_r + \alpha_s \boldsymbol{R}_s}{\alpha_r + \alpha_s}$. Then all the integrals needed are as follows[1]:

Overlap integral:

$$S_{pq} = \langle \chi_p | \chi_q \rangle = \left(\frac{4\alpha_p \alpha_q}{(\alpha_p + \alpha_q)^2}\right)^{\frac{3}{4}} \exp\left(\frac{-\alpha_p \alpha_q}{\alpha_p + \alpha_q} |\boldsymbol{R}_p - \boldsymbol{R}_q|^2\right). \tag{P.1}$$

Kinetic energy integral:

$$T_{pq} = \left\langle \chi_p \left| -\frac{1}{2}\Delta \right| \chi_q \right\rangle = \frac{\alpha_p \alpha_q}{\alpha_p + \alpha_q} \left(3 - \frac{2\alpha_p \alpha_q}{\alpha_p + \alpha_q} |\boldsymbol{R}_p - \boldsymbol{R}_q|^2\right) S_{pq}. \tag{P.2}$$

Nuclear attraction integral[2]*:*

$$V_{pq}^{\alpha} = \left\langle \chi_p \left| \frac{1}{|\boldsymbol{r} - \boldsymbol{R}_\alpha|} \right| \chi_q \right\rangle = 2\sqrt{\frac{\alpha_p + \alpha_q}{\pi}} F_0\left((\alpha_p + \alpha_q)|\boldsymbol{R}_\alpha - \boldsymbol{R}_k|^2\right) S_{pq}. \tag{P.3}$$

[1] S.F. Boys, *Proc. Roy. Soc. (London)*, *A200*, 542 (1950).

[2] In order to interpret this integral (in atomic units) as the Coulombic attraction of the electronic charge $\chi_p^*(1)\chi_q(1)$ by the nucleus (of charge Z, located at $\boldsymbol{R}_\alpha$), we have to multiply the integral by $-Z$.

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Electron repulsion integral:

$$\begin{aligned}(pr|qs) = (\chi_p\chi_r|\chi_q\chi_s) &= \int \chi_p(1)^*\chi_q(1)\frac{1}{r_{12}}\chi_r^*(2)\chi_s(2)dv_1dv_2 \\ &= \frac{2}{\sqrt{\pi}}\frac{\sqrt{\alpha_p+\alpha_q}\sqrt{\alpha_r+\alpha_s}}{\sqrt{\alpha_p+\alpha_q+\alpha_r+\alpha_s}}F_0\left(\frac{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)}{\alpha_p+\alpha_q+\alpha_r+\alpha_s}|\boldsymbol{R}_k-\boldsymbol{R}_l|^2\right)S_{pq}S_{rs}, \quad \text{(P.4)}\end{aligned}$$

with F_0 defined as[3]

$$F_0(t) = \frac{1}{\sqrt{t}}\int_0^{\sqrt{t}}\exp(-u^2)\mathrm{d}u. \quad \text{(P.5)}$$

Note that for an atom (all the centers coincide), we have $t = 0$ and $F_0(0) = 1$.

Do These Formulas Work?

The formulas look quite complex. If they are correct, they have to work in several simple situations. For example, if the electronic distribution $\chi_p^*(1)\chi_q(1)$ centered at $\boldsymbol{R}_k$ was far away from the nucleus, then as a matter of fact, we had to obtain the Coulombic interaction of the charge of $\chi_p^*(1)\chi_q(1)$ and the nucleus. The total charge of the electron cloud $\chi_p^*(1)\chi_q(1)$ is obviously equal to S_{pq}, and therefore $\frac{S_{pq}}{|\boldsymbol{R}_\alpha-\boldsymbol{R}_k|}$ should be a very good estimation of the nuclear attraction integral, right?

What we need is the asymptotic form of $F_0(t)$, if $t \to \infty$. This can be deduced from our formula for $F_0(t)$. The integrand is concentrated close to $t = 0$. For $t \to \infty$, the contributions to the integral become negligible and the integral itself can be replaced by $\int_0^\infty \exp(-u^2)\mathrm{d}u = \sqrt{\pi}/2$. This gives $\left[F_0(t)\right]_{asympt.} = \frac{\sqrt{\pi}}{2\sqrt{t}}$ and $\left(V_{pq}^\alpha\right)_{asympt.} = 2\sqrt{\frac{\alpha_p+\alpha_q}{\pi}}F_0\left((\alpha_p+\alpha_q)|\boldsymbol{R}_\alpha-\boldsymbol{R}_k|^2\right)$ $S_{pq} = 2\sqrt{\frac{\alpha_p+\alpha_q}{\pi}}\frac{\sqrt{\pi}}{2\sqrt{(\alpha_p+\alpha_q)|\boldsymbol{R}_\alpha-\boldsymbol{R}_k|^2}}S_{pq} = \frac{S_{pq}}{|\boldsymbol{R}_\alpha-\boldsymbol{R}_k|}$, exactly what we have expected. If $\chi_p = \chi_q$, then $S_{pq} = 1$ and we get simply the Coulombic law for the unit charges. It works!

Similarly, if in the electronic repulsion integral $\chi_p = \chi_q$, $\chi_r = \chi_s$, and the distance $|\boldsymbol{R}_k - \boldsymbol{R}_l| = R$ is large, then what we should get is the Coulombic law for the two pointlike unit charges at distance R. Let us see. Asymptotically,

$$\begin{aligned}(pr|qs)_{asympt.} &= \frac{2}{\sqrt{\pi}}\frac{\sqrt{\alpha_p+\alpha_q}\sqrt{\alpha_r+\alpha_s}}{\sqrt{\alpha_p+\alpha_q+\alpha_r+\alpha_s}}F_0\left(\frac{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)}{\alpha_p+\alpha_q+\alpha_r+\alpha_s}|\boldsymbol{R}_k-\boldsymbol{R}_l|^2\right) \\ &= \frac{2}{\sqrt{\pi}}\frac{\sqrt{\alpha_p+\alpha_q}\sqrt{\alpha_r+\alpha_s}}{\sqrt{\alpha_p+\alpha_q+\alpha_r+\alpha_s}}\frac{\sqrt{\pi}}{2\sqrt{\frac{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)}{\alpha_p+\alpha_q+\alpha_r+\alpha_s}}|\boldsymbol{R}_k-\boldsymbol{R}_l|^2} = \frac{1}{R},\end{aligned}$$

which is exactly what we should obtain.

[3] The values of $F_0(t)$ are reported in L.J. Schaad, G.O. Morrell, *J. Chem. Phys.*, *54*, 1965 (1971).