P. MOLECULAR INTEGRALS WITH GAUSSIAN TYPE ORBITALS 1s

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

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

The molecular integrals usually involve, at most, four such orbitals: $\chi_p, \chi_q, \chi_r, \chi_s$, with corresponding centres $\boldsymbol{R}_p, \boldsymbol{R}_q, \boldsymbol{R}_r, \boldsymbol{R}_s$, and exponents $\alpha_p, \alpha_q, \alpha_r, \alpha_s$, respectively. Since any product of the 1s GTOs represents a (non-normalized) 1s GTO centred between the centres of the individual GTOs (see p. 359), let us denote the centre 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 centre 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]

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

electron repulsion integral:

$$\begin{aligned}(pr|qs) = (\chi_p\chi_r|\chi_q\chi_s) &= \int \chi_p(1)^*\chi_q(1)\frac{1}{r_{12}}\chi_r^*(2)\chi_s(2)\,\mathrm{d}v_1\,\mathrm{d}v_2 \\ &= \frac{2}{\sqrt{\pi}}\frac{\sqrt{\alpha_p+\alpha_q}\sqrt{\alpha_r+\alpha_s}}{\sqrt{\alpha_p+\alpha_q+\alpha_r+\alpha_s}}F_0\left(\frac{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)}{\alpha_p+\alpha_q+\alpha_r+\alpha_s}|\boldsymbol{R}_k-\boldsymbol{R}_l|^2\right)S_{pq}S_{rs}\end{aligned} \tag{P.4}$$

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

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

with F_0 defined as[3]

$$F_0(t) = \frac{1}{\sqrt{t}} \int_0^{\sqrt{t}} \exp\bigl(-u^2\bigr)\,\mathrm{d}u. \tag{P.5}$$

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

Do these formulae work?

The formulae look quite complex. If they are correct, they have to work in several simple situations. For example, if the electronic distribution $\chi_p^*(1)\chi_q(1)$ centred at $\boldsymbol{R}_k$ is far away from the nucleus, then we have 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 $[F_0(t)]_{\text{asympt.}} = \frac{\sqrt{\pi}}{2\sqrt{t}}$ and

$$\begin{aligned}\bigl(V_{pq}^{\alpha}\bigr)_{\text{asympt.}} &= 2\sqrt{\frac{\alpha_p + \alpha_q}{\pi}} F_0\bigl((\alpha_p + \alpha_q)|\boldsymbol{R}_\alpha - \boldsymbol{R}_k|^2\bigr) S_{pq} \\ &= 2\sqrt{\frac{\alpha_p + \alpha_q}{\pi}} \frac{\sqrt{\pi}}{2\sqrt{(\alpha_p + \alpha_q)|\boldsymbol{R}_\alpha - \boldsymbol{R}_k|^2}} S_{pq} = \frac{S_{pq}}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_k|},\end{aligned}$$

exactly as we expected. If $\chi_p = \chi_q$, then $S_{pq} = 1$ and we simply get 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 we should get the Coulombic law for the two point-like unit charges at distance R. Let us see. Asymptotically

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

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 (1971) 1965.