9 Evaluation of two-centre integrals

The integrals required in the discussion of the hydrogen molecular ion can all be obtained from the basic integral

$$\mathcal{J} = \int \frac{e^{-pr_A} e^{-qr_B}}{r_A r_B} \, d\mathbf{r} \tag{A9.1}$$

where $\mathbf{r}$, $\mathbf{r}_A$ and $\mathbf{r}_B$ are defined in Fig. 9.8.

This integral is most easily evaluated by introducing confocal elliptic coordinates defined by (see [9.59])

$$\begin{aligned} \xi &= \frac{1}{R}(r_A + r_B), \qquad 1 \leqslant \xi \leqslant \infty \\ \eta &= \frac{1}{R}(r_A - r_B), \qquad -1 \leqslant \eta \leqslant 1 \end{aligned} \tag{A9.2}$$

and ϕ, the azimuthal angle about the Z axis. We recall that the quantity R which appears in [A9.2] is the internuclear separation. The volume element $d\mathbf{r}$, expressed in terms of the confocal elliptic coordinates (ξ, η, ϕ), is given by

$$d\mathbf{r} = \frac{R^3}{8}(\xi^2 - \eta^2) \, d\xi \, d\eta \, d\phi \tag{A9.3}$$

so that

$$\mathcal{J} = \frac{R}{2} \int_1^\infty d\xi \int_{-1}^{+1} d\eta \int_0^{2\pi} d\phi \, e^{-a\xi - b\eta} \tag{A9.4}$$

where

$$\begin{aligned} a &= \frac{R}{2}(p + q) \\ b &= \frac{R}{2}(p - q) \end{aligned} \tag{A9.5}$$

The integral [A9.4] is now elementary and is given by

$$\mathcal{J} = \frac{\pi R}{ab} e^{-a}(e^{b} - e^{-b})$$

$$= \frac{4\pi}{R} \frac{1}{p^2 - q^2} (e^{-qR} - e^{-pR}) \qquad [A9.6]$$

The other relevant integrals are obtained by differentiating the above result with respect to p and q. That is,

$$K = \int \frac{e^{-pr_A} e^{-qr_B}}{r_A} d\mathbf{r} = -\frac{\partial}{\partial q} \mathcal{J}$$

$$= \frac{4\pi}{R} \left[\frac{R}{p^2 - q^2} e^{-qR} + \frac{2q}{(p^2 - q^2)^2} (e^{-pR} - e^{-qR}) \right] \qquad [A9.7]$$

and

$$L = \int e^{-pr_A} e^{-qr_B} d\mathbf{r} = -\frac{\partial}{\partial p} K$$

$$= \frac{8\pi}{R(p^2 - q^2)^2} \left[R(pe^{-qR} + qe^{-pR}) + \frac{4pq}{p^2 - q^2} (e^{-pR} - e^{-qR}) \right] \qquad [A9.8]$$

In the particular case $p = q$, we have

$$\mathcal{J} = \frac{2\pi}{p} e^{-pR} \qquad [A9.9]$$

$$K = \frac{\pi}{p^2} (1 + pR) e^{-pR} \qquad [A9.10]$$

and

$$L = \frac{\pi}{p^3} \left(1 + pR + \frac{1}{3} p^2 R^2 \right) e^{-pR} \qquad [A9.11]$$