Appendix K: Direct and exchange integrals for helium

The direct integral differs from the integral $D0$ evaluated in Box 11.1 only in using the hydrogenic wavefunction $\langle\mathbf{x}'|200\rangle$ instead of $\langle\mathbf{x}'|100\rangle$ for $\Psi_2(\mathbf{x}')$. Comparing the forms of $\langle\mathbf{x}'|100\rangle$ and $\langle\mathbf{x}'|200\rangle$ given in Table 8.1, we see that equation (1) of Box 11.1 becomes

$$D = \frac{1}{4a_Z^3}\int \mathrm{d}^3\mathbf{x}_1\,|\Psi_{10}^0(\mathbf{x}_1)|^2\int \mathrm{d}r_2\mathrm{d}\theta_2\frac{r_2^2(1-r_2/2a_Z)^2\sin\theta_2\mathrm{e}^{-r_2/a_Z}}{\sqrt{|r_1^2+r_2^2-2r_1r_2\cos\theta_2|}}. \qquad \text{(K.1)}$$

After integrating over θ as in Box 11.1, we again break the integral over r_2 into two parts, and have

$$\begin{aligned} D &= \frac{1}{2a_Z^3}\int \mathrm{d}^3\mathbf{x}_1\,|\Psi_{10}^0(\mathbf{x}_1)|^2\left\{\int_0^{r_1}\mathrm{d}r_2\,\frac{r_2^2}{r_1}\left(1-\frac{r_2}{2a_Z}\right)^2\mathrm{e}^{-r_2/a_Z}\right.\\ &\qquad\left.+\int_{r_1}^{\infty}\mathrm{d}r_2\,r_2\left(1-\frac{r_2}{2a_Z}\right)^2\mathrm{e}^{-r_2/a_Z}\right\}\\ &= \frac{1}{2a_Z}\int \mathrm{d}^3\mathbf{x}_1\,|\Psi_{10}^0(\mathbf{x}_1)|^2\left\{\frac{a_Z}{r_1}\int_0^x \mathrm{d}\rho\,(\rho^2-\rho^3+\tfrac14\rho^4)\mathrm{e}^{-\rho}\right.\\ &\qquad\left.+\int_x^\infty \mathrm{d}\rho\,(\rho-\rho^2+\tfrac14\rho^3)\mathrm{e}^{-\rho}\right\}, \end{aligned}$$

where $\rho\equiv r_2/a_Z$ and $x=r_1/a_Z$. Now

$$\int_a^b \mathrm{d}\rho\,\rho^n\mathrm{e}^{-\rho} = n\int_a^b \mathrm{d}\rho\,\rho^{n-1}-[\rho^n\mathrm{e}^{-\rho}]_a^b,$$

so

$$\int_a^b \mathrm{d}\rho\,(\rho^2-\rho^3+\tfrac14\rho^4)\mathrm{e}^{-\rho} = \int_a^b \mathrm{d}\rho\,\rho^2-\tfrac14[\rho^4\mathrm{e}^{-\rho}]_a^b = -[(2+2\rho+\rho^2+\tfrac14\rho^4)\mathrm{e}^{-\rho}]_a^b,$$

and

$$\begin{aligned} \int_a^b \mathrm{d}\rho\,(\rho-\rho^2+\tfrac14\rho^3)\mathrm{e}^{-\rho} &= \int_a^b \mathrm{d}\rho\,(\rho-\tfrac14\rho^2)\mathrm{e}^{-\rho}-\tfrac14[\rho^3\mathrm{e}^{-\rho}]_a^b\\ &= \tfrac12\int_a^b \mathrm{d}\rho\,\rho-\tfrac14[(-\rho^2+\rho^3)\mathrm{e}^{-\rho}]_a^b\\ &= -\tfrac14[(2+2\rho-\rho^2+\rho^3)\mathrm{e}^{-\rho}]_a^b. \end{aligned}$$

Thus taking Ψ_{10}^0 from Table 8.1,

$$\begin{aligned} D &= \frac{1}{2a_Z}\int \mathrm{d}^3\mathbf{x}_1\,|\Psi_{10}^0(\mathbf{x}_1)|^2\left\{\frac{1}{x}[2-(2+2x+x^2+\tfrac14x^4)\mathrm{e}^{-x}]\right.\\ &\qquad\left.+\tfrac14[(2+2x-x^2+x^3)\mathrm{e}^{-x}]\right\}\\ &= \frac{2}{a_Z}\int_0^\infty \mathrm{d}x\,x^2\mathrm{e}^{-2x}\frac{1}{4x}\{8-(8+6x+2x^2+x^3)\mathrm{e}^{-x}\}\\ &= \frac{1}{2a_Z}\left\{8\int_0^\infty \mathrm{d}x\,x\mathrm{e}^{-2x}-\int_0^\infty \mathrm{d}x\,(8x+6x^2+2x^3+x^4)\mathrm{e}^{-3x}\right\}\\ &= \frac{1}{2a_Z}\{2-(\tfrac89+\tfrac29\,2!+\tfrac{2}{3^4}3!+\tfrac{1}{3^5}4!)\} = \frac{1}{2a_Z}\{2-\tfrac{12}{9}-\frac{3!}{3^4}(2+\tfrac43)\}\\ &= \frac{1}{2a_Z}(\tfrac23-\tfrac{20}{81}) = \frac{17}{81a_Z}. \end{aligned} \qquad \text{(K.2)}$$

Exchange integral Similarly,

$$E = \frac{1}{\sqrt{2}a_Z^3}\int d^3\mathbf{x}_1\, \Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^0(\mathbf{x}_1)\int dr_2 d\theta_2 \frac{r_2^2(1 - r_2/2a_Z)\sin\theta_2 e^{-3r_2/2a_Z}}{\sqrt{|r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2|}}. \tag{K.3}$$

After integrating over θ as in Box 11.1, we have

$$\begin{aligned}
E &= \frac{\sqrt{2}}{a_Z^3}\int d^3\mathbf{x}_1\, \Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^0(\mathbf{x}_1)\left\{\int_0^{r_1} dr_2\, \frac{r_2^2}{r_1}\left(1 - \frac{r_2}{2a_Z}\right)e^{-3r_2/2a_Z}\right.\\
&\qquad\qquad \left. + \int_{r_1}^\infty dr_2\, r_2\left(1 - \frac{r_2}{2a_Z}\right)e^{-3r_2/2a_Z}\right\}\\
&= \frac{\sqrt{2}}{a_Z}\int d^3\mathbf{x}_1\, \Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^0(\mathbf{x}_1)\left\{\frac{a_Z}{r_1}(\tfrac{2}{3})^3\int_0^{3x/2} d\rho\,(\rho^2 - \tfrac{1}{3}\rho^3)e^{-\rho}\right.\\
&\qquad\qquad \left. + (\tfrac{2}{3})^2\int_{3x/2}^\infty d\rho\,(\rho - \tfrac{1}{3}\rho^2)e^{-\rho}\right\},
\end{aligned}$$

where $\rho \equiv 3r_2/2a_Z$ and $x = r_1/a_Z$. Now

$$\int_a^b d\rho\,(\rho^2 - \tfrac{1}{3}\rho^3)e^{-\rho} = \tfrac{1}{3}[\rho^3 e^{-\rho}]_a^b$$

and

$$\int_a^b d\rho\,(\rho - \tfrac{1}{3}\rho^2)e^{-\rho} = \tfrac{1}{3}\int_a^b d\rho\,\rho e^{-\rho} + \tfrac{1}{3}[\rho^2 e^{-\rho}]_a^b = -\tfrac{1}{3}[(1 + \rho - \rho^2)e^{-\rho}]_a^b.$$

Thus

$$\begin{aligned}
E &= \frac{\sqrt{2}}{a_Z}\int d^3\mathbf{x}_1\, \Psi_{10}^{0*}(\mathbf{x}_1)\Psi_{20}^0(\mathbf{x}_1)\left\{\frac{1}{x}(\tfrac{2}{3})^3\tfrac{1}{3}(\tfrac{3}{2}x)^3 e^{-3x/2}\right.\\
&\qquad\qquad \left. + (\tfrac{2}{3})^2\tfrac{1}{3}(1 + \tfrac{3}{2}x - (\tfrac{3}{2}x)^2)e^{-3x/2}\right\}\\
&= \frac{2}{3a_Z}\int dx\, x^2(1 - \tfrac{1}{2}x)e^{-3x/2}\{x^2 e^{-3x/2} + ((\tfrac{2}{3})^2 + \tfrac{2}{3}x - x^2)e^{-3x/2}\}\\
&= \frac{4}{9a_Z}\int dx\,(x^2 - \tfrac{1}{2}x^3)(\tfrac{2}{3} + x)e^{-3x} = \frac{4}{9a_Z}\int dx\,(x^3 - \tfrac{1}{2}x^4 - \tfrac{1}{3}x^3 + \tfrac{2}{3}x^2)e^{-3x}\\
&= \frac{4}{9a_Z}\int dx\,(\tfrac{2}{3}x^3 - \tfrac{1}{2}x^4 + \tfrac{2}{3}x^2)e^{-3x} = \frac{4}{9a_Z}\int d\rho\,(\tfrac{2}{3^5}\rho^3 - \tfrac{1}{2\times 3^5}\rho^4 + \tfrac{2}{3^4}\rho^2)e^{-\rho}\\
&= \frac{4}{9a_Z}\frac{1}{3^5}(2\times 3! - \tfrac{1}{2}4! + 6\times 2!) = \frac{2^4}{3^6 a_Z}.
\end{aligned}$$

The bottom line Given that $a_Z = \frac{1}{2}a_0$ and $\frac{e^2}{4\pi a_0} = 2\mathcal{R}$, our estimates of the energies of the singlet and triplet states are

$$E_\pm = -5\mathcal{R} + \frac{e^2}{4\pi a_Z}\left(\frac{17}{3^4} \pm \frac{2^4}{3^6}\right) = -\left(5 - \frac{68}{3^4} \mp \frac{2^6}{3^6}\right)\mathcal{R} = -(56.6 \mp 1.19)\,\text{eV}.$$