Engel 9.3

Problem. Show that the 100 and 200 hydrogen atom wave functions are orthogonal. These wave functions are eigenfunctions of the total energy operator, so they must be orthogonal, but the idea here is to demonstrate this principle.

Answer. I just need to write the wave functions in spherical polar coordinates and carry out a three-variable integration over the product of the two functions (overlap integral). Remember that integrations in spherical polar coordinates require that the integrand be multiplied by $r^2 \sin\theta \, \mathrm{dr} \, \mathrm{d}\theta \, \mathrm{d}\phi$. Also, normalization constants can be ignored because we are expecting the overlap integral to vanish.

$$\psi 100 = e^{-r/a0}$$
$$\psi 200 = \left(2 - \frac{r}{a0}\right) e^{-r/(2\,a0)}$$

$$e^{-\frac{r}{a0}}$$

$$e^{-\frac{r}{2\,a0}} \left(2 - \frac{r}{a0}\right)$$

Integrating with respect to *r* ...

$$\int_0^\infty \psi 100 \, \psi 200 \, r^2 \, dr$$

$$\text{If}\left[\text{Re}[a0] > 0,\ 0,\ \text{Integrate}\left[-\frac{e^{-\frac{3\,r}{2\,a0}}\, r^2\, (-2\,a0 + r)}{a0},\ \{r, 0, \infty\},\ \text{Assumptions} \to \text{Re}[a0] \le 0\right]\right]$$

This integral vanishes because a0 is the Bohr radius and is greater than 0. The remaining integrals do not need to be evaluated because, whatever their value, the product of the three integrals will be zero and this is what we expect for orthogonal functions.