Engel 9.4

Problem. Show that the 210 and 211 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. A second part of the question asks whether it is necessary to carry out integrations with respect to all three spatial variables to settle this question.

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.

$$\psi210 = \left(\frac{r}{a0}\right) e^{-r/(2\,a0)} \,\mathrm{Cos}[\theta]$$

$$\psi211 = \left(\frac{r}{a0}\right) e^{-r/(2\,a0)} \,\mathrm{Sin}[\theta]\, e^{i\,\phi}$$

$$\frac{e^{-\frac{r}{2\,a0}}\, r\, \mathrm{Cos}[\theta]}{a0}$$

$$\frac{e^{-\frac{r}{2\,a0}+i\,\phi}\, r\, \mathrm{Sin}[\theta]}{a0}$$

Integrating with respect to r ...

$$\int_0^\infty \psi210\, \psi211\, r^2\, dr$$

$$\frac{1}{a0^2}\,(\mathrm{Cos}[\theta]\ \mathrm{If}[\mathrm{Re}[a0] > 0,\ 24\, a0^5\, e^{i\,\phi},$$
$$\mathrm{Integrate}[e^{-\frac{r}{a0}+i\,\phi}\, r^4,\ \{r, 0, \infty\},\ \mathrm{Assumptions} \to \mathrm{Re}[a0] \le 0]]\ \mathrm{Sin}[\theta])$$

Rintegral = Simplify[%, a0 > 0]

$$24\, a0^3\, e^{i\,\phi}\, \mathrm{Cos}[\theta]\, \mathrm{Sin}[\theta]$$

Integration with respect to r leads to a non-zero result, so we proceed by integrating with respect to θ ...

$$\int_0^\pi \mathrm{Rintegral}\ \mathrm{Sin}[\theta]\, d\theta$$

0

At this point the overlap integral vanishes, which establishes the orthogonality of the two wave functions. You might wonder what would happen had we integrated with respect to ϕ first ...

$$\int_0^{2\pi} \textbf{Rintegral}\, d\phi$$

0

The overlap integral vanishes again. Both of the angular integrals vanish. We can see why this occurs by inspecting the following graphs. The second and third functions are odd functions, so their integrals must vanish.

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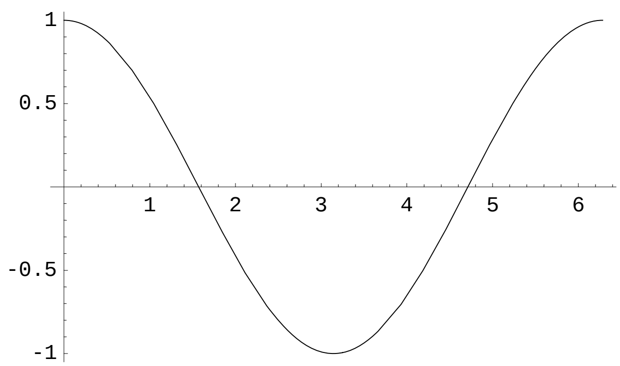
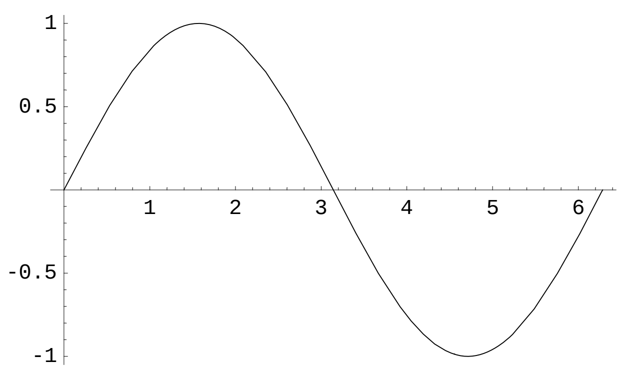
Plot[Re[e^(i ϕ)], {ϕ, 0, 2 π}]
```



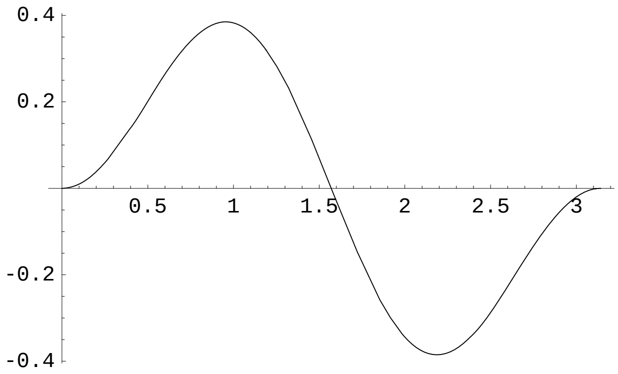
- Graphics -

```
Plot[Im[e^(i ϕ)], {ϕ, 0, 2 π}]
```



- Graphics -

```
Plot[Cos[θ] Sin[θ]^2, {θ, 0, π}]
```

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