Announcements

- Homework 7 is due TODAY.
- Homework 8 is due next Wednesday, March 29.

Last time

- Wave function of the hydrogen atom

Today’s class

- Probability density

in-class quiz (2 min)

Which hydrogen wavefunction is valid for (n,l,m_l)?

a. (3,2,3)
b. (3,3,1)
c. (2,4,–4)
d. (2,5,4)
e. (3,1,1)

in-class quiz (2 min)

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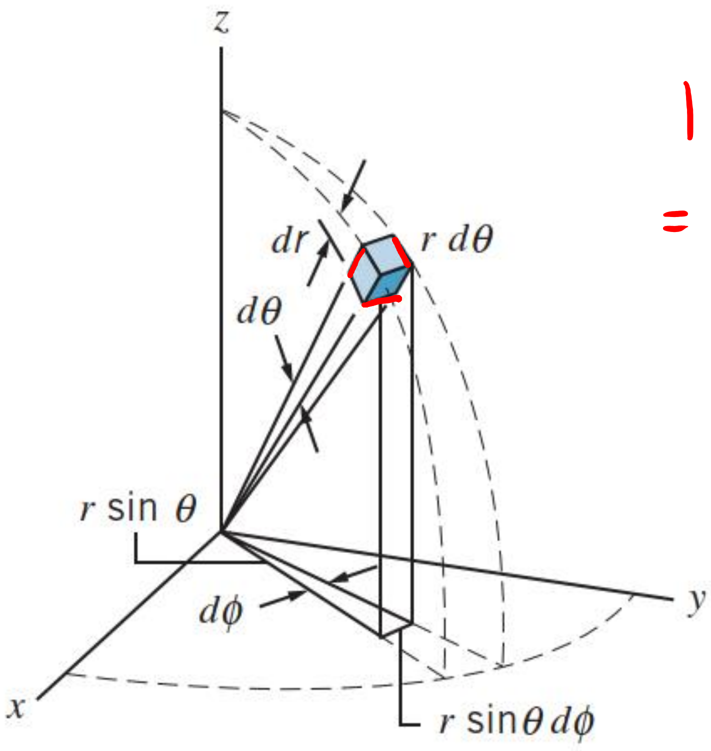
n

$l = 0, \cdots, n-1$

$m_l = 0, \pm 1, \cdots, \pm l$

Volume probability density



$$dV = dr \cdot r\,d\theta \cdot r\sin\theta\,d\phi$$
$$= r^2 \sin\theta\,dr\,d\theta\,d\phi$$

$$|\psi_{n,l,m_l}(r,\theta,\phi)|^2 dV$$
$$= |R_{n,l}(r)|^2 |\Theta_{l,m_l}(\theta)|^2 |\Phi_{m_l}(\phi)|^2\, r^2 \sin\theta\,dr\,d\theta\,d\phi$$

Radial probability density

The probability to find the electron in the shell between spheres of radius $\underline{\underline{r}}$ and $\underline{\underline{r+dr}}$

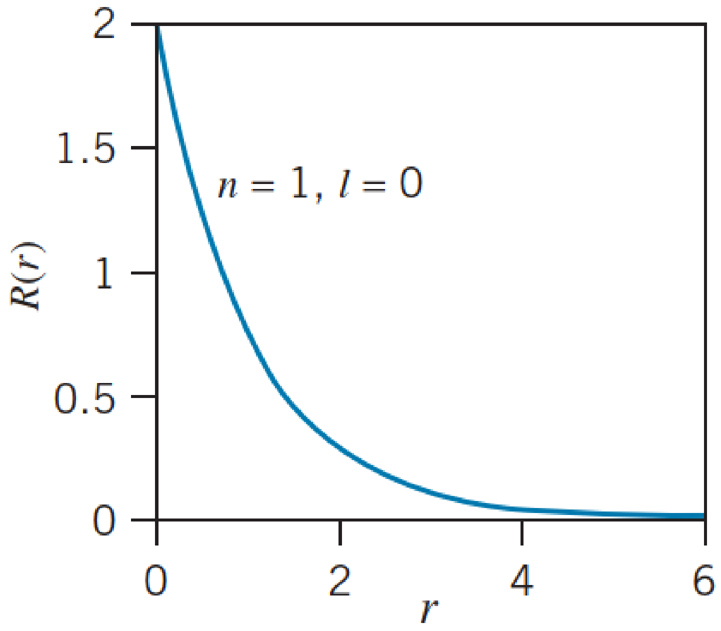
Probability density is probability per unit length dr $\quad P(r)$

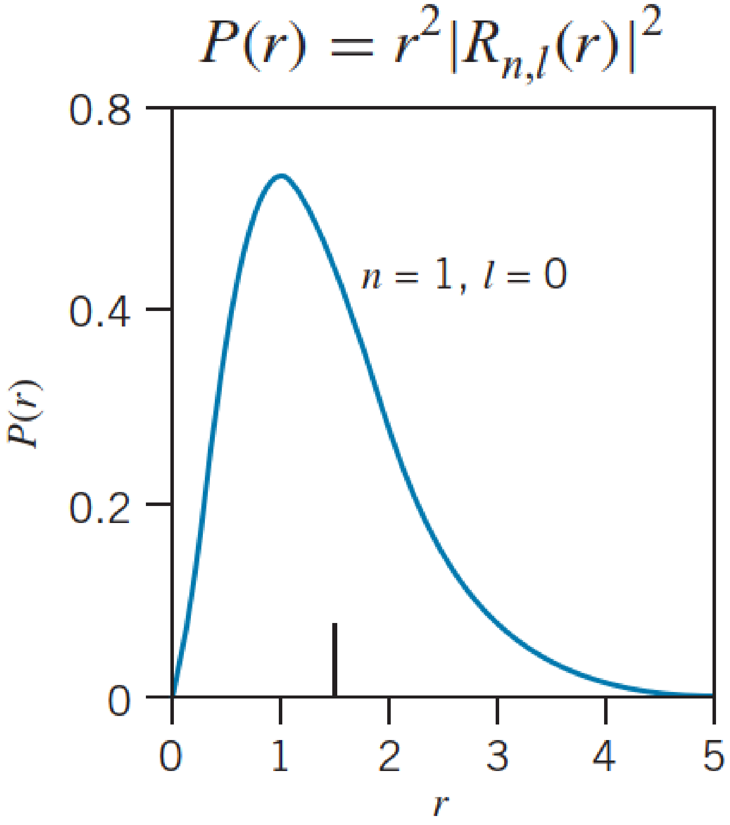
$$P(r)dr = |R_{n,l}(r)|^2 r^2 dr \underbrace{\int_0^{\pi} |\Theta_{l,m_l}(\theta)|^2 \sin\theta \, d\theta}_{1} \underbrace{\int_0^{2\pi} |\Phi_{m_l}(\phi)|^2 d\phi}_{1}$$

$$= |R_{n,l}(r)|^2 r^2 dr$$

$$\boxed{P(r) = r^2 |R_{n,l}(r)|^2}$$

Compare P(r) and R(r)





in-class exercise (10 min)

For state n=2, *l*=1.

n	l	m_l	$R(r)$	$\Theta(\theta)$	$\Phi(\phi)$
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\sqrt{\frac{3}{2}} \cos\theta$	$\frac{1}{\sqrt{2\pi}}$

a. What is the most probable radius?

b. What is the expectation value (i.e. average value) of the radius? Hints: https://www.integral-calculator.com/

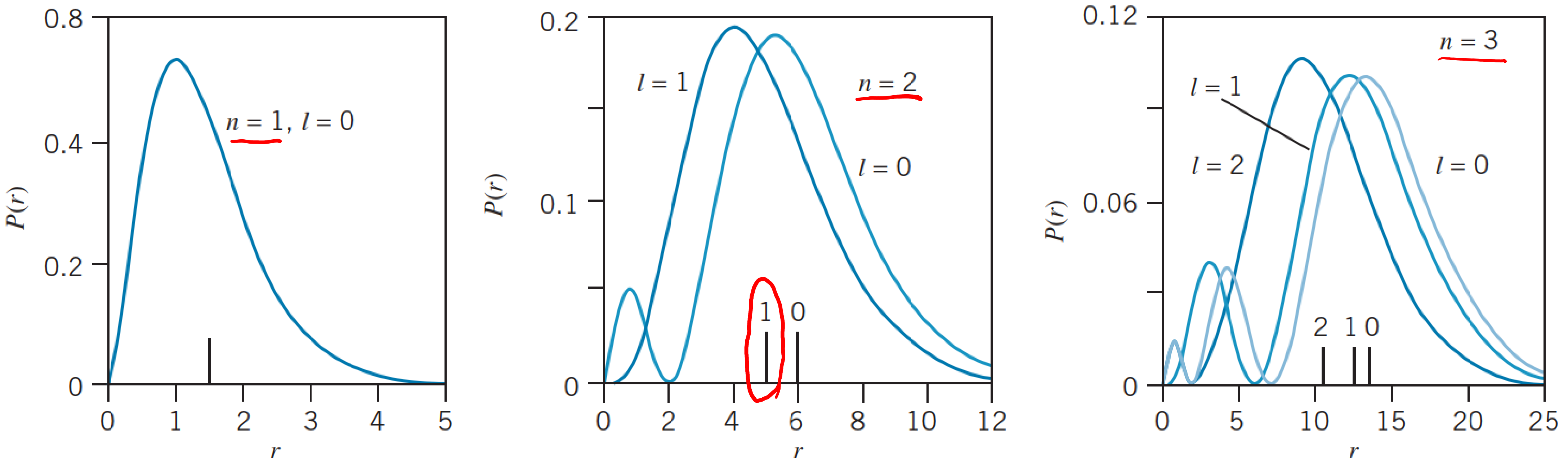
c. Compare your answers in part a and part b.

a. $P(r) = r^2 |R(r)|^2 = r^2 \cdot \frac{1}{3 \cdot 8a_0^3 \, a_0^2} r^2 e^{-r/a_0} = \frac{r^4 e^{-r/a_0}}{24 a_0^5}$

$\frac{dP(r)}{dr} = \frac{1}{24a_0^5}\left[4r^3 e^{-r/a_0} + r^4 e^{-r/a_0}\left(-\frac{1}{a_0}\right)\right] = \frac{1}{24a_0^5} \cdot r^3 e^{-r/a_0}\left(4 - \frac{r}{a_0}\right) = 0$

$r = 0$, $r = \infty$, $\boxed{r = 4a_0}$

b. $r_{av} = \int_0^\infty r P(r) dr = \int_0^\infty r^3 |R(r)|^2 dr = \frac{1}{24a_0^5} \int_0^\infty r^5 e^{-r/a_0} dr = \frac{1}{24a_0^5} 120 a_0^6 = \underline{5a_0}$



1. The x scale is different. Average radius is marked. Which affects the average radius more, n or *l* ?

2. Recall which quantum number affects the energy?

Angular probability density

$$P(\theta, \phi) = |\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)|^2$$

cylindrically symmetric—there is no dependence on the azimuthal angle Φ.

n	l	m_l	$R(r)$	$\Theta(\theta)$	$\Phi(\phi)$
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$
2	1	±1	$\frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\mp\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$

Find the direction in space at which the maximum probability occurs when $m_l = 0$ and when $m_l = \pm1$.

$|e^{\pm i\phi}|^2 = 1$

$m_l = 0$ $\quad P(\theta,\phi) = |\Theta(\theta)\Phi(\phi)|^2 = \frac{3}{4\pi}\cos^2\theta$

$\frac{dP}{d\theta} = \frac{3}{4\pi}(-2\cos\theta\sin\theta) = 0$ $\to \cos\theta = 0, \ \theta = \frac{\pi}{2}$

$\to \boxed{\sin\theta = 0, \ \theta = 0 \text{ or } \pi}$

$\frac{d^2P}{d\theta^2} = \frac{3}{2\pi}(1 - 2\cos^2\theta)$ $\quad \cos\theta = 0, \ \frac{d^2P}{d\theta^2} = \frac{3}{2\pi}$

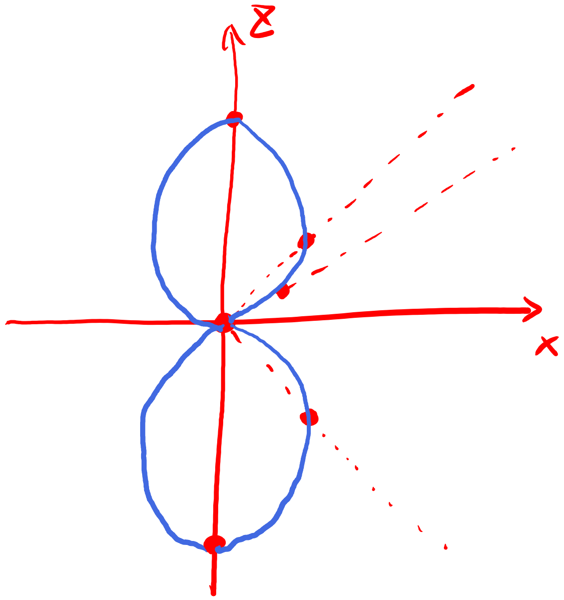
$\sin\theta = 0, \ \cos^2\theta = 1, \ \frac{d^2P}{d\theta^2} = -\frac{3}{2\pi}$, maximum

$m_l = \pm1$ $\quad P(\theta,\phi) = \frac{3}{8\pi}\sin^2\theta$, $\quad \frac{dP}{d\theta} = \frac{3}{4\pi}\sin\theta\cos\theta = 0$

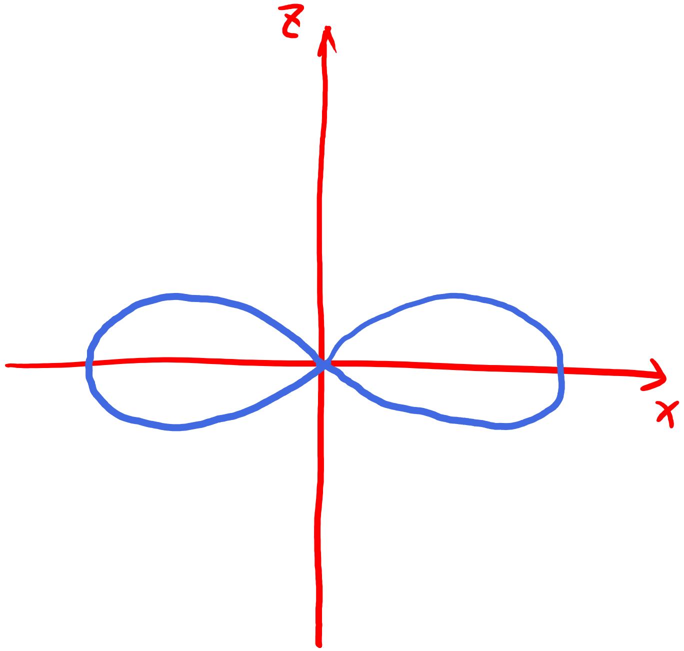
$\cos\theta = 0, \ \frac{d^2P}{d\theta^2} < 0$, maximum, $\quad \theta = \frac{\pi}{2}$

$\cos^2\theta$

θ	$\cos^2\theta$
0	1
45°	$\frac{1}{2}$
60°	$\frac{1}{4}$
90°	0
135°	$\frac{1}{2}$
180°	1



$\sin^2\theta$



Angular probability density