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mass m in 3D box $L_1 \times L_2 \times L_3$

Find six lowest energy states when $L_1 = L$, $L_2 = 2L$, $L_3 = 2L$.

Indicate which of these are degenerate.

The 3D particle in a box is covered in Section 8.1

Most of this discussion focuses on the case of $L_1 = L_2 = L_3 = L$.

We have to back up to the formulae:

$$E = \frac{1}{2m} (|p_x|^2 + |p_y|^2 + |p_z|^2) = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_1^2}{L^2} + \frac{n_2^2}{(2L)^2} + \frac{n_3^2}{(2L)^2} \right)$$
$$= \frac{\pi^2 \hbar^2}{2mL^2} \left(n_1^2 + \frac{n_2^2}{4} + \frac{n_3^2}{4} \right)$$

We are looking for the 6 lowest states.

n_1	n_2	n_3	E
1	1	1	$\frac{\pi^2 \hbar^2}{2mL^2} \left(1 + \frac{1}{4} + \frac{1}{4} \right)$
1	2	1	$\frac{\pi^2 \hbar^2}{2mL^2} \left(1 + 1 + \frac{1}{4} \right)$
1	1	2	$\frac{\pi^2 \hbar^2}{2mL^2} \left(1 + \frac{1}{4} + 1 \right)$
1	2	2	$\frac{\pi^2 \hbar^2}{2mL^2} \left(1 + 1 + 1 \right)$
1	1	3	$\frac{\pi^2 \hbar^2}{2mL^2} \left(1 + \frac{1}{4} + \frac{9}{4} \right)$
1	3	1	$\frac{\pi^2 \hbar^2}{2mL^2} \left(1 + \frac{9}{4} + \frac{1}{4} \right)$

Notice that raising the "n" corresponding to y and z is less "energy costly" than in the x direction because the box is bigger in those directions. Also, because some of the directions are the same size, some combinations of n values give the same energy. These states are called "degenerate".

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3D box with $L_1 = L_2 = L_3 = L$, mass m in $n^2 = 11$

What is the energy of the particle?

$$\text{Equation 8.9 } E = \frac{\pi^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2) = \frac{\pi^2 \hbar^2}{2mL^2} (1^2 + 1^2 + 3^2) = \boxed{\frac{11\pi^2 \hbar^2}{2mL^2}}$$

(b) What combinations of n_s will give this energy?

$n_1 \ n_2 \ n_3$

(i) 1 1 3 }

(ii) 1 3 1 } all of these give $n^2 = 11$

(iii) 3 1 1 }

(c) The wavefunctions are given by Equation 8.10

$$\psi(x, y, z, t) = \left(\frac{2}{L}\right)^{3/2} \sin(k_1 x) \sin(k_2 y) \sin(k_3 z) e^{-i\omega t}$$

$$(i) k_3 = \frac{3\pi}{L}, k_1 = k_2 = \frac{\pi}{L}$$

$$(ii) k_2 = \frac{3\pi}{L}, k_1 = k_3 = \frac{\pi}{L}$$

$$(iii) k_1 = \frac{3\pi}{L}, k_2 = k_3 = \frac{\pi}{L}$$

#4 p. 1

2D box $L \times L$

What are the wave functions?

The wave functions for 1D, 2D and 3D boxes are almost the same except for the normalization constant.

$$\psi(x, y) = \left(\frac{2}{L}\right) \sin\left(\frac{n_1 \pi}{L} x\right) \sin\left(\frac{n_2 \pi}{L} y\right)$$

$n_1 = n_2 = 1$ gives the ground state ← not degenerate

$n_1 = 1, n_2 = 2$ or $n_1 = 2, n_2 = 1$ gives the first excited state

↑

degenerate

$$\text{with } E_n = \frac{\pi^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2)$$

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3D box w/ $L = 2 \times 10^{-14} \text{ m}$, $m = m_p$ (proton)

What is the ground state energy?

$$E_n = \frac{\pi^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$$

$$n_1 = n_2 = n_3 = 1 \Rightarrow E = 1.54 \text{ MeV}$$

What are the energies of the first and second excited states?

$$n_1 = 2, n_2 = n_3 = 1 \Rightarrow E = 3.08 \text{ MeV}$$

$$n_1 = 2, n_2 = 2, n_3 = 1 \Rightarrow E = 4.63 \text{ MeV}$$

What are the degeneracies?

Note that in both cases, you can have 3 combinations of n_s will give that energy. \Rightarrow 3-fold degenerate

#7 p. 1

The normalization condition is

$$\int_0^{L_1} \int_0^{L_2} \int_0^{L_3} |\Psi(x, y, z)|^2 dx dy dz = 1$$

This is not as bad as it looks because the wavefunctions are real and separable, so the integral can be rewritten:

$$A^2 \int_0^{L_1} \sin^2(k_1 x) dx \int_0^{L_2} \sin^2(k_2 y) dy \int_0^{L_3} \sin^2(k_3 z) dz = 1$$

Obviously all of these integrals will be the same, so

$$\int_0^{L_1} \sin^2(k_1 x) dx = \int_0^{L_1} \left(\frac{1}{2} - \frac{1}{2} \cos(2k_1 x) \right) dx = \left[\frac{x}{2} - \frac{1}{4k_1} \sin(2k_1 x) \right]_0^{L_1} = \frac{L_1}{2}$$

$$\text{so we get } A = \sqrt{\frac{2}{L_1}} \sqrt{\frac{2}{L_2}} \sqrt{\frac{2}{L_3}} = \sqrt{\frac{8}{V}} \text{ where } V = \text{volume } (L_1 \times L_2 \times L_3)$$

$$\text{For } L_1 = L_2 = L_3 = L, A = \left(\frac{2}{L}\right)^{3/2}$$

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electron $n=4, l=3, m_l = 3$

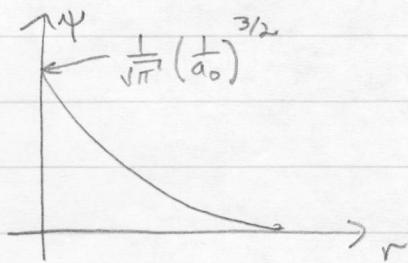
What is the orbital angular momentum?

$$\text{Equation 8.16} \therefore |L| = \sqrt{l(l+1)\hbar} = \sqrt{3(3+1)}\hbar = 3.65 \times 10^{-34} \text{ Js}$$
$$L_z = m_l \hbar = 3\hbar = 3.16 \times 10^{-34} \text{ Js}$$

#12 p.1

ground-state of hydrogen $\Psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

(a) Sketch Ψ versus r



(b) This is basically a calculus question: look up 3D integrals in spherical polar coordinates. Note that the integrals over θ and ϕ are easy because the wave function does not depend on those coordinates.

The probability is given by $|\Psi|^2 dV$. For any given r , this dV corresponds to a spherical shell, the volume of which is given by $dV = 4\pi r^2 dr$

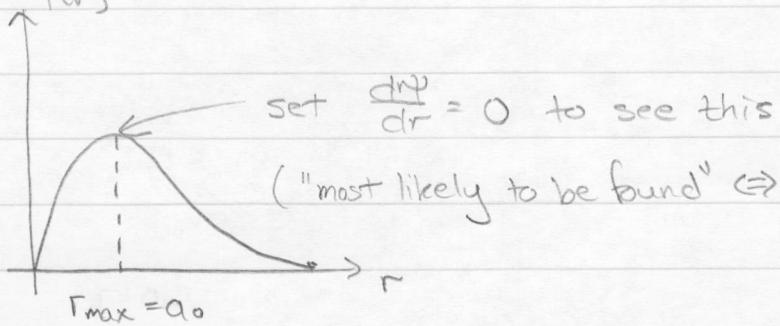
$$P = |\Psi|^2 4\pi r^2 dr$$

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(c) Sketch $P(r)$ versus r and find r_{\max}

Note that $P(r) \rightarrow 0$ as $r \rightarrow \infty$ because $P(r) \propto r^2 e^{-r/a_0}$

$P(r)$



$$(d) 4\pi \int_0^\infty |\psi|^2 r^2 dr = \frac{4\pi}{\pi a_0^3} \int_0^\infty e^{-2r/a_0} r^2 dr = 1$$

use integration by parts,
your calculator, computer,
integral table or Professor
(but not your TA)

$$(e) P = \int_{r_1=a_0/2}^{r_2=3a_0/2} \frac{4}{a_0^3} e^{-2r/a_0} r^2 dr = -\frac{17}{2} e^{-3} + \frac{5}{2} e^{-1} \approx 0.496$$

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$$\mu = \frac{mM}{m+M}, \text{ Equation 8.38 : } E_n = -\frac{k e^2}{2a_0} \left\{ \frac{z^2}{n^2} \right\}$$

$$a_0 = \frac{\pi^2}{m_e e^2 k}, \text{ change } \mu \leftrightarrow m_e \Rightarrow E_n = -\frac{\mu k^2 e^4}{2\pi^2} \left\{ \frac{z^2}{n^2} \right\}$$

(b) For an $n=3 \rightarrow n=2$ transition,

$$E_3 - E_2 = \frac{hc}{\lambda} = -\frac{\mu k^2 e^4 z^2}{2\pi^2} \left\{ \frac{1}{3^2} - \frac{1}{2^2} \right\}$$

$$\begin{aligned} \text{if } z=1 \text{ (Hydrogen)} &\Rightarrow \lambda \approx 656.3 \text{ nm} \\ \text{if } z=2 \text{ (Helium)} &\Rightarrow \lambda \approx 164.1 \text{ nm} \end{aligned} \quad \left. \begin{array}{l} \text{for these, } \mu=m_e \\ \text{if } z=1 \text{ and } \mu=\frac{m_e}{2} \text{ (positronium)} \Rightarrow \lambda \approx 1312.6 \text{ nm} \end{array} \right.$$

#16 p.1

Calculate the possible values of the z component of angular momentum for an electron in a d subshell.

d subshell $\Rightarrow l=2 \Rightarrow m_l = -2, -1, 0, 1, 2; L_z = m_l \hbar$

#17 p.1

Calculate L for 4d and 6f electrons in hydrogen.

$$L = \sqrt{l(l+1)} \hbar$$

$$4d \Rightarrow l=2 \Rightarrow L = 2.58 \times 10^{-34} \text{ Js}$$

$$6f \Rightarrow l=3 \Rightarrow L = 3.65 \times 10^{-34} \text{ Js}$$