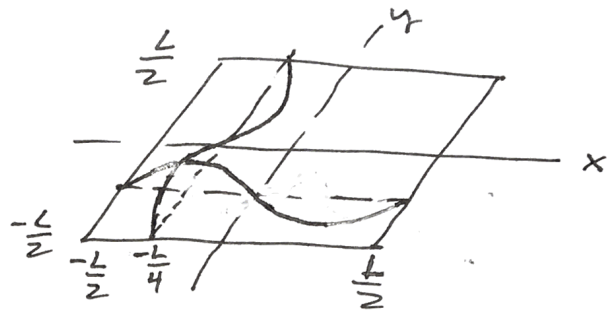


Problem 1

$$\Psi(x, y) = A \sin(k_1(x + \frac{L}{2})) \sin(k_2(y + \frac{L}{2}))$$

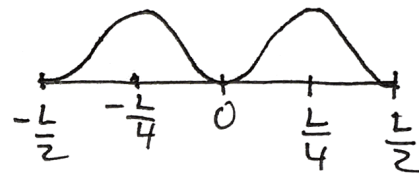


so that  $\Psi(x = -\frac{L}{2}, y) = \Psi(x, y = -\frac{L}{2}) = 0$

and we need  $\Psi(x = \frac{L}{2}, y) = \Psi(x, y = \frac{L}{2}) = 0$  which requires

$$k_1 = \frac{n_1 \pi}{L}, \quad k_2 = \frac{n_2 \pi}{L}, \quad n_1, n_2 \text{ integers.}$$

The probability is maximal for  $x = y = \frac{L}{4} \Rightarrow$



$$\Rightarrow \boxed{n_1 = 2, n_2 = 2}$$

The energy is  $E_{n_1, n_2} = \frac{\hbar^2 \pi^2}{2m_e L^2} (n_1^2 + n_2^2) = \frac{7.62 \times \pi^2}{2 \times 25} \times 8 \text{ eV} = 12.03 \text{ eV}$

(b) so  $\boxed{E_{22} = 12.03 \text{ eV}}$

(2,3) (3,2)	_____	10
2,2	_____	8
(2,1); (1,2)	↑↓ ↑↓	5
1,1	↑↓	2
$n_1, n_2$		$n_1^2 + n_2^2$

the closest state with higher energy is (1,3) or (3,1) transition to that state will absorb longest wavelength photon.

$$\frac{hc}{\lambda} = E_{3,1} - E_{2,2} = \frac{7.62 \times \pi^2}{50} (10 - 8) \text{ eV}$$

$$\Rightarrow \boxed{\lambda = \frac{12,400 \text{ \AA}}{3.008} = 4122 \text{ \AA}}$$

(c) shortest wavelength photon emitted:  $\frac{hc}{\lambda} = E_{3,2} - E_{1,1} = \frac{7.62 \pi^2}{50} (8 - 2) \text{ eV}$

$$\Rightarrow \boxed{\lambda = 1374 \text{ \AA}}$$

(d) Occupy all lower states with electrons

$$\boxed{\text{need 6 electrons}}$$

## Problem 2

$$\Psi(r, \theta, \phi) = C \cdot r \cdot e^{-3r/a_0} e^{i m_e \phi} \cos \theta$$

(a) The exponential is always of the form  $e^{-zr/a_0}$

$\Rightarrow \frac{z}{n} = 3$ . From the fact that the wavefunction has no nodes

and the fact  $r^l$  we deduce that  $n=2$  and  $l=1$ . Therefore,  $z=6$

From the  $\cos \theta$  factn we deduce that  $m_l=0$

(b) Radial probability:  $P(r) = r^2 R(r)^2 = C^2 r^4 e^{-6r/a_0}$

Most probable  $r$ :  $P'(r) = 0 = 4r^3 - \frac{6r^4}{a_0} \Rightarrow r = \frac{2}{3} a_0$

(c)  $U(r) = -\frac{ke^2 z}{r}$

$$\langle \frac{1}{r} \rangle = \frac{\int_0^\infty dr \frac{1}{r} P(r)}{\int_0^\infty dr P(r)} = \frac{\int_0^\infty dr r^3 e^{-6r/a_0}}{\int_0^\infty dr r^4 e^{-6r/a_0}} = \frac{3! 6^5}{6^4 \cdot 4! a_0} = \frac{6}{4a_0} = \frac{3}{2a_0}$$

$$\Rightarrow \langle U(r) \rangle = -\frac{ke^2 \cdot 6 \cdot 3}{2a_0} = -\frac{9ke^2}{a_0}$$

(d) For the Bohr atom, with  $n=2$ :

$$r_n = \frac{a_0 n^2}{z} = \frac{a_0 \cdot 2^2}{6} = \frac{2}{3} a_0 \text{ agrees with (b)}$$

$$U(r) = -\frac{ke^2 z}{r_n} = -\frac{ke^2 \cdot 6}{\frac{2}{3} a_0} = -\frac{9ke^2}{a_0} \text{ agrees with (c)}$$

### Problem 3

In the presence of a magnetic field, the energy of level  $n$  is

$$E_n(B) = E_n - \vec{\mu} \cdot \vec{B} = E_n - \mu_z B$$

If only spin,  $\mu_z = -\frac{e\hbar}{2m_e} m_l = -\mu_B m_l \Rightarrow$

$$E_n(B) = E_n + \mu_B B m_l. \text{ So for the transition } 3d \text{ to } 2p:$$

$$E_3(B) = E_3 + \mu_B B m_{3l}, \quad E_2(B) = E_2 + \mu_B B m_{2l}$$

$$\Rightarrow E_3(B) - E_2(B) = E_3 - E_2 + \mu_B B (\underbrace{m_{3l} - m_{2l}}_{\Delta m_l})$$

$m_{3l} = \pm 2, \pm 1, 0$  and  $m_{2l} = \pm 1, 0$ . However because of the selection rule  $\Delta m_l = \pm 1$  or  $0$  there are only 3 possible photons, with

$$\text{wavelengths: } \lambda_1 = \frac{hc}{E_3 - E_2}, \quad \lambda_2 = \frac{hc}{E_3 - E_2 + \mu_B B}, \quad \lambda_3 = \frac{hc}{E_3 - E_2 - \mu_B B}$$

$$E_3 - E_2 = 1.889 \text{ eV}, \quad \mu_B B = 5.79 \times 10^{-4} \text{ eV} \Rightarrow$$

$$(a) \quad \lambda_1 = 6564.3 \text{ \AA}, \quad \lambda_2 = 6562.3 \text{ \AA}, \quad \lambda_3 = 6566.3 \text{ \AA}$$

(b) With spin,  $\mu_z = -\mu_B (m_l + 2m_s)$ ,  $m_s = \pm \frac{1}{2}$

$$E_3(B) - E_2(B) = E_3 - E_2 + \mu_B B (m_{3l} + 2m_{3s} - m_{2l} - 2m_{2s})$$

$$= E_3 - E_2 + \mu_B B \left( \underbrace{(m_{3l} + m_{3s}) - (m_{2l} + m_{2s})}_{= \Delta(m_l + m_s) = 0, 1, \text{ or } -1} + \underbrace{m_{3s} - m_{2s}}_{\substack{\text{max value} = 1 \\ \text{min value} = -1}} \right)$$

So maximum <sup>and minimum</sup> difference is:  $E_3 - E_2 \pm 2\mu_B B$

$$\Rightarrow \lambda_{\max} = \frac{hc}{E_3 - E_2 - 2\mu_B B} = 6568.3 \text{ \AA}$$
$$\lambda_{\min} = \frac{hc}{E_3 - E_2 + 2\mu_B B} = 6560.3 \text{ \AA}$$