Quantum Mechanics in 2D & 3D

Note Title 3/21/2017

Electron in hydrogen roams in 3D under the potential $U(\vec{r}) = -\frac{ke^2}{r}$

So we need to consider TISE in 3D:

$$-\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) + U(x,y,z)\,\psi(x,y,z) = E\,\psi(x,y,z)$$

or $$\underbrace{\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)}_{\frac{\partial^2}{\partial x^2}\psi + \frac{\partial^2}{\partial y^2}\psi + \frac{\partial^2}{\partial z^2}\psi} = \frac{2M}{\hbar^2}\left(U(x,y,z) - E\right)\psi(x,y,z)$$

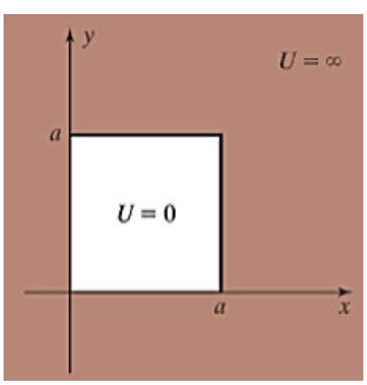
Example 8.1

Find the three partial derivatives $\partial\psi/\partial x$, $\partial\psi/\partial y$, and $\partial\psi/\partial z$ for $\psi(x, y, z) = x^2 + 2y^3z + z$.

$$\frac{\partial\psi}{\partial x} = 2x, \quad \frac{\partial\psi}{\partial y} = 6y^2z, \quad \frac{\partial\psi}{\partial z} = 2y^3 + 1$$

TISE in 2D:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} = \frac{2M}{\hbar^2}\left(U(x,y) - E\right)\psi(x,y)$$



The straightforward extension of the rigid box to 2D:

$$U(x,y) = \begin{cases} 0, & \text{inside box } x \in (0,a) \ \& \ y \in (0,a) \\ \infty & \text{outside} \end{cases}$$

$0 \le E < \infty$, accordingly we can write $E = \frac{\hbar^2 k_x^2}{2M} + \frac{\hbar^2 k_y^2}{2M}$

To solve for $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} = -\frac{2M}{\hbar^2}E\,\psi$ inside. We will use the method of "separation of variables" which we used to reduce TDSE to TISE.

Set $\psi(x,y) = X(x)\, Y(y)$

then. $Y \frac{d^2 X}{dx^2} + X \frac{d^2 Y}{dy^2} = -\frac{2M}{\hbar^2} E\, X Y$

$\Rightarrow$ divide both sides by XY

$$\frac{1}{X}\frac{d^2 X}{dx^2} + \frac{1}{Y}\frac{d^2 Y}{dy^2} = -\frac{2M}{\hbar^2} E = \text{const indep. of } x \,\&\, y$$

$\Rightarrow$ $\underset{-k_x^2}{\underset{|||}{\frac{1}{X}\frac{d^2X}{dx^2}}}$ & $\underset{-k_y^2}{\underset{|||}{\frac{1}{Y}\frac{d^2Y}{dy^2}}}$ are constants.

[satisfy boundary condition 0 at $x = 0, a$]

From 1-d case. we know that $X_{n_x}(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}$ $n_x = 1, 2, 3, \ldots$

$Y_{n_y}(y) = \sqrt{\frac{2}{a}} \sin \frac{n_y \pi y}{a}$ $n_y = 1, 2, 3, \ldots$

$$\left\{ \begin{array}{l} k_x = \frac{n_x \pi}{a} \\ k_y = \frac{n_y \pi}{a} \end{array} \right.$$

Eigen functions (stationary solutions) are (labeled by n_x & n_y)

$\psi_{n_x, n_y}(x,y) = \frac{2}{a} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{a}$ and they are properly normalized

$\int_0^a dx \int_0^a dy \left| \psi_{n_x, n_y}(x,y) \right|^2 = 1$ easy to see that $\psi_{n_x, n_y}(x,y) = 0$ on wall

$\sin \frac{n_x \pi x}{a} = \frac{1}{2i} \left(e^{i \frac{n_x \pi}{a} x} - e^{-i \frac{n_x \pi}{a} x} \right)$ comes from adding two counter-propagating free-particle wave functions with $p_x = \pm \hbar \frac{n_x \pi}{a}$

$\sin \frac{n_y \pi y}{a}$ " y " y $\Rightarrow$ $p_y = \pm \hbar \frac{n_y \pi}{a}$

n_x & n_y are called quantum numbers

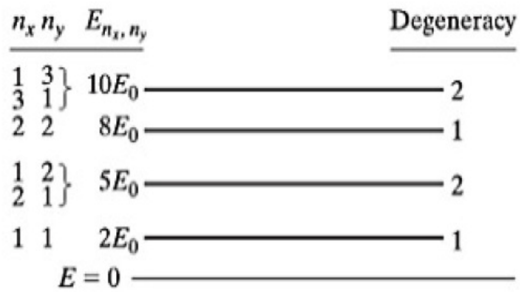
$$E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2M}(n_x^2+n_y^2) \equiv E_0\,(n_x^2+n_y^2), \quad E_0 \equiv \frac{\hbar^2\pi^2}{2M}$$

- lowest energy $n_x = n_y = 1$, $E_{1,1} = 2E_0$
- the first excited states $(n_x=1, n_y=2)$ or $(n_x=2, n_y=1)$, $E_{1,2} = E_{2,1} = 5E_0$

with different
$$\begin{cases} \psi_{1,2}(x,y) = \frac{2}{a}\sin\frac{\pi x}{a}\sin\frac{2\pi y}{a} \\ \psi_{2,1}(x,y) = \frac{2}{a}\sin\frac{2\pi x}{a}\sin\frac{\pi y}{a} \end{cases}$$
$\Rightarrow$ this is called degenerate

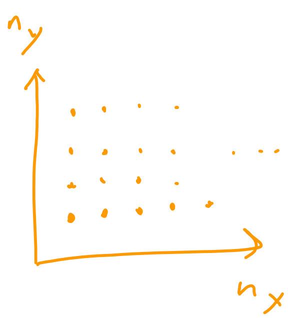
FIGURE 8.2

The energy levels of a particle in a two-dimensional, square rigid box. The lowest allowed energy is $2E_0$; the line at $E = 0$ is merely to show the zero of the energy scale. The degeneracies, listed on the right, refer to the number of independent wave functions with the same energy.



$N > 1$ independent wave functions with the same energy E.

Nondegenerate if only one w.f. for that energy.

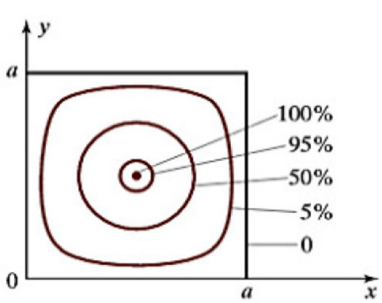


e.g. $E_{5,5} = E_{1,7} = E_{7,1}$ $\quad 5^2+5^2 = 1^2+7^2$

e.g. $E_{1,8} = E_{8,1} = E_{4,7} = E_{7,4}$ $\quad 1^2+8^2 = 4^2+7^2$

[degeneracy will have important effect on atomic structure and chemical properties.]

Contour of $|\psi(x,y)|^2$



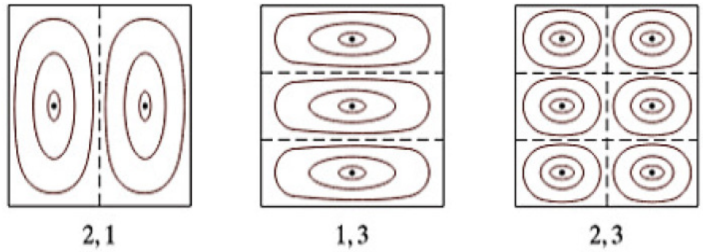
$$|\psi_{1,1}(x,y)|^2 = \left(\frac{2}{a}\right)^2 \sin^2\frac{\pi x}{a}\,\sin^2\frac{\pi y}{a}.$$

FIGURE 8.3

Contour map of the probability density $|\psi|^2$ for the ground state of the square box. The percentages shown give the value of $|\psi|^2$ as a percentage of its maximum value.

FIGURE 8.4

Contour maps of $|\psi|^2$ for three excited states of the square box. The two numbers under each picture are n_x and n_y. The dashed lines are nodal lines, where $|\psi|^2$ vanishes; these occur where ψ passes through zero as it oscillates from positive to negative values.



Example 8.2

Having solved the Schrödinger equation for a particle in the two-dimensional square box, one can solve the corresponding three-dimensional problem very easily. (See Problem 8.15.) The result is that the allowed energies for a mass M in a rigid cubical box of side a have the form

$$E = E_0(n_x^2 + n_y^2 + n_z^2) \tag{8.32}$$

where $E_0 = \hbar^2\pi^2/(2Ma^2)$ is the same energy introduced in (8.28), and the quantum numbers n_x, n_y, n_z are any three positives integers. Use this result to find the lowest five energy levels and their degeneracies for a mass M in a rigid cubical box of side a.

(1,1,1) deg = 1 $\quad E = 3E_0$

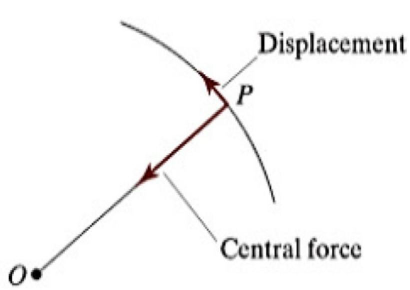
(1,1,2), (1,2,1), (2,1,1) deg = 3 $\quad E = 6E_0$

(1,2,2) (2,1,2) (2,2,1) deg = 3 $\quad E = 9E_0$

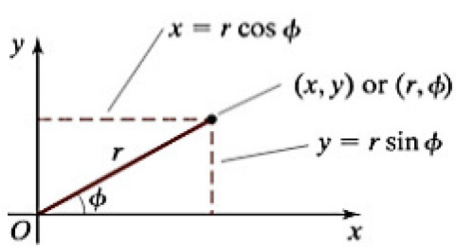
(1,1,3), (1,3,1), (3,1,1) deg = 3 $\quad E = 11E_0$

(2,2,2) deg = 1 $\quad E = 12E_0$

2D Central force problem



For a central force, the potential $U(r)$ only depends on the radius to the origin not the angle φ.



One can take advantage of this lack of dependence, which is a symmetry in the problem.

To exploit the symmetry one needs to use the appropriate coordinate (r, ϕ) and write the wavefcn as a fcn of (r, ϕ) instead of (x, y)

The relation between the two: $\begin{cases} x = r\cos\phi \\ y = r\sin\phi \end{cases}$

We need to convert $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$ to the expression using only r & ϕ

which turns out to be

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$$

$$\left[\text{also notice that } \frac{\partial^2}{\partial r^2}\psi + \frac{1}{r}\frac{\partial}{\partial r}\psi = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) \right]$$

So TISE becomes

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r}\frac{\partial \psi}{\partial r} + \frac{1}{r^2}\frac{\partial^2 \psi}{\partial \phi^2} = \frac{2M}{\hbar^2}\left[U(r) - E \right]\psi$$

The next step is to use separation of variables

$$\psi(r, \phi) \equiv R(r)\,\Phi(\phi)$$

then

$$\Phi(\phi)\frac{d^2R(r)}{dr^2} + \Phi(\phi)\frac{1}{r}\frac{dR(r)}{dr} + \frac{1}{r^2}R(r)\frac{d^2\Phi}{d\phi^2} = \frac{2M}{\hbar^2}\left[U(r) - E \right] R(r)\,\Phi(\phi)$$

$\Rightarrow$ divide both sides by ΦR and multiply by r^2

$$r^2\left(\frac{R''(r)}{R(r)} + \frac{1}{r}\frac{R'(r)}{R(r)} \right) + \frac{\Phi''(\phi)}{\Phi} = \frac{2M}{\hbar^2} r^2 \left(U(r) - E \right)$$

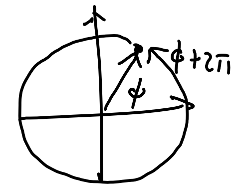
i.e. $$\underbrace{\frac{\Phi''(\phi)}{\Phi}}_{\text{function of } \phi} = \underbrace{-r^2\left(\frac{R''(r)}{R(r)} + \frac{1}{r}\frac{R'(r)}{R(r)} \right) + \frac{2M}{\hbar^2} r^2 \left[U(r) - E \right]}_{\text{function of } r} \Longrightarrow -m^2$$

constant indep of (r, ϕ)

$$\boxed{\Phi''(\phi) = -m^2\,\Phi(\phi)}$$ [we have seen this $\psi''(x) = -k^2\psi(x)$]

↳ solutions $\Phi(\phi) = e^{\pm im\phi}$ $\overset{\text{take}}{\Rightarrow} e^{im\phi}$ (if we allow m to be either + or − we can take $e^{im\phi}$)

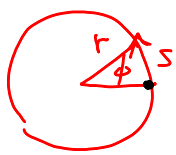
Since $\phi \to \phi + 2\pi \Rightarrow$ same location



require $\psi(r,\phi) = \psi(r, \phi+2\pi)$

so $e^{im\phi} = e^{im\phi + im2\pi} \Rightarrow e^{i2m\pi} = 1 \Rightarrow \underbrace{m \text{ integer} = 0, \pm 1, \pm 2, \cdots}_{}$

this is quantization of angular momentum



$\phi = \frac{s}{r}$

s: measured arc distance from x axis

$\Rightarrow e^{im\phi} = e^{i\frac{m}{r}s} \Longleftrightarrow e^{ik\cdot x}$ linear momentum $p = \hbar k$

momentum p_ϕ (along arc) $= \frac{\hbar m}{r}$, angular mom. $L_z \equiv r\,p_\phi = \hbar m$

quantized in unit of $\hbar$!

The other part is

$$\frac{r^2R'' + rR'}{R} - \frac{2Mr^2}{\hbar^2}(U(r) - E) = m^2$$

$$\Rightarrow R'' + \frac{R'}{r} - \left[\frac{m^2}{r^2} + \frac{2M}{\hbar^2}(U(r) - E)\right]R = 0$$

energy has a label m [quantum #]

For this part we need to require $R(r) \xrightarrow[r\to\infty]{} 0$

$\Rightarrow$ This will give us quantization of energy $\Rightarrow$ another quantum # say n

$\Rightarrow E_{n,m}$

Since the above equation depends on m^2, we expect $E_{n,-m} = E_{n,m}$

Also we expect excited states will have nodes in $R(r)$!

To go one step more we have $R'' + \frac{R'}{r} = \frac{1}{r}\frac{d^2(rR)}{dr^2}$

So $\frac{d^2}{dr^2}(rR) - \left(\frac{m^2}{r^2} + \frac{2M}{\hbar^2}(U(r) - E) \right)(rR) = 0$

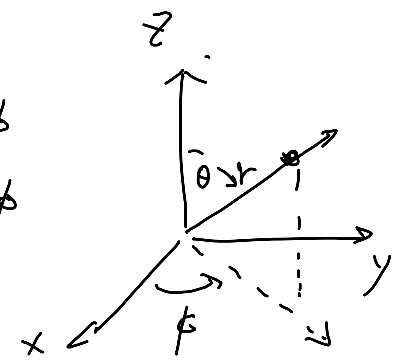
Comparing to 1d: $\frac{d^2}{dx^2}\psi - \frac{2M}{\hbar^2}[V(x) - E]\psi = 0$

we can identify $\begin{cases} \psi(x) \longleftrightarrow rR(r) \\ V(x) \longleftrightarrow U(r) + \frac{\hbar^2}{2M}\frac{m^2}{r^2} \end{cases}$

But this is as far as we can go in this course.

With the above preparation, we will now discuss 3D Central-force problem.

① we need coordinate change: $\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases}$



② $\nabla^2\psi$ is more complicated

$$\nabla^2\psi \equiv \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

$$\nabla^2\psi(r,\theta,\phi) = \frac{2M}{\hbar^2}[U(r) - E]\psi$$

Next step: separation of variable $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$

Compared to 2D case we have one more variable θ.

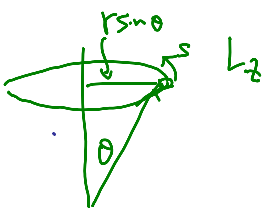
Plug $\psi = R\Theta\Phi$ in TISE

$$\frac{1}{r}\frac{d^2}{dr^2}(rR(r))\Theta\Phi + \frac{R}{r^2}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\Phi + \frac{R}{r^2}\frac{\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2}$$

$$= \frac{2M}{\hbar^2}\left[U(r) - E\right] R\, \Theta\, \Phi .$$

① divide both sides by $\dfrac{R\,\Theta\,\Phi}{r^2 \sin^2\theta}$ to isolate $\dfrac{d^2\Phi}{d\phi^2 \, \Phi}$

$$\frac{r}{R}\frac{d^2}{dr^2}(rR)\sin^2\theta + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{} = \frac{2M}{\hbar^2}\left[U - E\right] r^2 \sin^2\theta$$



$e^{im\phi} = e^{im\frac{s}{r\sin\theta}}$

$P_\phi = \frac{\hbar m}{r\sin\theta}$ $\quad L_z = r\sin\theta\, P_\phi = m\hbar$

↳ function of ϕ only = function of r & θ

quantization of L_z angular momentum $\Leftarrow$ m integer $\Longleftarrow$ $\dfrac{1}{\Phi}\dfrac{d^2\Phi}{d\phi^2} = -m^2$ (just like before)

② next is to replace $\dfrac{1}{\Phi}\dfrac{d^2\Phi}{d\phi^2}$ by $-m^2$.

$$\frac{r}{R}\frac{d^2}{dr^2}(rR)\sin^2\theta + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) - m^2 = \frac{2M}{\hbar^2}\left[U - E\right] r^2 \sin^2\theta$$

θ & r $\qquad$ θ $\qquad$ θ & r

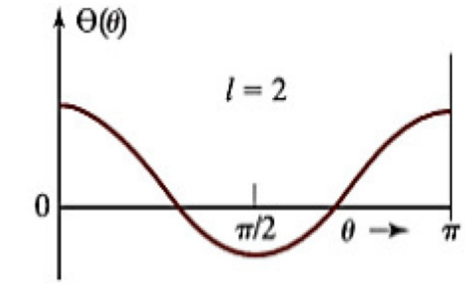
try to separate θ & r $\Rightarrow$ divide both sides by $\sin^2\theta$

$$\Rightarrow \underbrace{\frac{r}{R}\frac{d^2}{dr^2}(rR)}_{\text{fcn of } r} + \underbrace{\frac{1}{\sin\theta\,\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{m^2}{\sin^2\theta}}_{\text{fcn of } \theta} = \underbrace{\frac{2M}{\hbar^2}\left[U(r) - E\right] r^2}_{\text{fcn of } r}$$

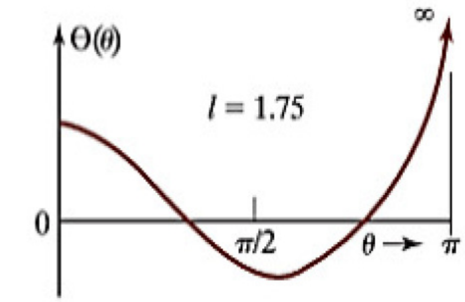
↳ must be a const. $\equiv -\ell(\ell+1)$ [ℓ is real & arbitrary @ this point]

$$\Rightarrow \begin{cases} \dfrac{d}{d\theta}\left(\sin\theta \dfrac{d\Theta}{d\theta}\right) - \sin\theta\left(\dfrac{m^2}{\sin^2\theta} - \ell(\ell+1)\right)\Theta = 0 \\[2ex] \dfrac{r}{R}\dfrac{d^2}{dr^2}(rR) - \ell(\ell+1) - \dfrac{2M}{\hbar^2}\left[U(r) - E\right] r^2 = 0 \end{cases}$$

Note that solutions for $\Phi(\phi)$ & $\Theta(\theta)$ is independent of $U(r)$.



(a)



(b)

For $\Theta(\theta)$ part, it turns out not all l's give solutions that are finite between $\theta \in [0, \pi]$

In order for $\Theta(\theta)$ to be finite, l is restricted to non-negative integers such that $l \geq |m|$

(or $m = -l, -l+1, \ldots, l-1, l$)

and we label the solution by $\Theta_{lm}(\theta)$

Since the radial equation depends on l and valid solutions lead to quantization of energy (that depends on l $\Rightarrow$ $E_{n,l}$)

n ↑ labels quantized energy; l ↑ fixed l

and radial w.f. $R_{nl}(r)$

Full

$\Rightarrow$ Solution $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,\Theta_{lm}(\theta)\, e^{im\phi}$

Angular momentum is a vector $\vec{L} = \vec{r} \times \vec{p}$

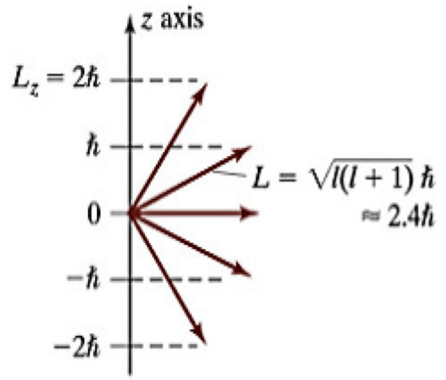
We have seen L_z is quantized $L_z = m\hbar$, it turns out that the magnitude of L is not $\underline{l}$ but $L = \sqrt{l(l+1)}\,\hbar$, $l = 0, 1, 2, 3, \ldots$ [l is a quantum #]

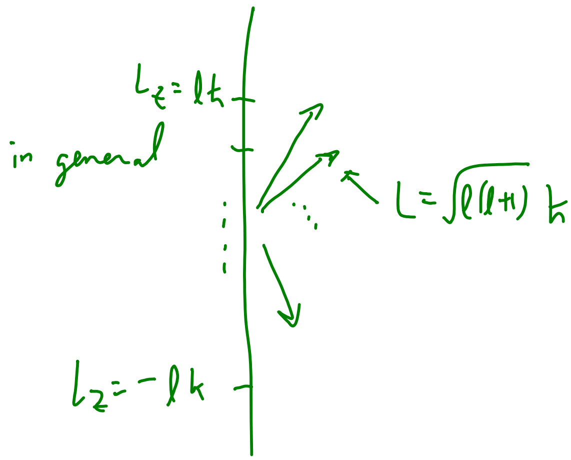
& $m = -l, -l+1, \ldots, l-1, l$

(large $l \Rightarrow L \approx l\hbar$)

Quantum number, l:	0	1	2	3	4	$\cdots$	l
Magnitude:	0	$\sqrt{2}\hbar$	$\sqrt{6}\hbar$	$\sqrt{12}\hbar$	$\sqrt{20}\hbar$	$\cdots$	$\sqrt{l(l+1)}\,\hbar$
compatible m's:	0	$-1, 0, 1$	$-2, -1, 0, 1, 2$	$-3, -2, \ldots 3$			
degeneracy [for fixed n & l]	1	3	5	7	8		$\boxed{2l+1}$

Vector model





Example 8.3

Write down the θ equation (8.53) for the cases that $l = 0$ and that $l = 1$, $m = 0$. Find the angular functions $\Theta_{lm}(\theta)e^{im\phi}$ explicitly for these two cases.

$m = 0$,

$$\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \sin\theta\,\big(l(l+1)\big)\Theta = 0$$

$l = 0$.

$$\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) = 0 \qquad \sin\theta \frac{d\Theta}{d\theta} = \text{Const} \qquad \frac{d\Theta}{d\theta} = \frac{c_1}{\sin\theta} \Rightarrow$$

$$\Rightarrow \Theta = \int \frac{c_1}{\sin\theta}\, d\theta \qquad \frac{d\theta}{2\sin\frac{\theta}{2}\cos\frac{\theta}{2}}$$

$$= c_1 \ln\left|\frac{\sin\frac{\theta}{2}}{\cos\frac{\theta}{2}}\right| + c_2$$

$$\frac{2\cdot\ d\sin\frac{\theta}{2}}{2\cos^2\frac{\theta}{2}\sin\frac{\theta}{2}} = \frac{dt}{t(1-t^2)}$$

$$= dt\,\frac{1}{t(1-t)(1+t)}$$

$$= \frac{1}{2}\frac{1}{t}\left(\frac{1}{1-t} + \frac{1}{1+t}\right)$$

$$\int = \frac{1}{2}\left[\frac{1}{t} + \frac{1}{1-t} + \frac{1}{t} - \frac{1}{1+t}\right]$$

$$\frac{1}{2}\ln\frac{t^2}{1-t^2}$$

$$= \cancel{\tfrac{1}{2}}\ \ln\frac{\sin\frac{\theta}{2}}{\cos\frac{\theta}{2}}$$

But if $c_1 \neq 0$. then as $\theta \to 0, \pi$

$\Theta \to \infty$

So we need to have $c_1 = 0$ i.e. $\Theta = \text{Const}$.

usually we take $\Theta_{00} = \frac{1}{\sqrt{4\pi}}$

$l = 1$.
$$\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + 2\sin\theta\ \Theta = 0$$

By inspection $\Theta = \cos\theta$ is a solution

The other solution is harder to find. and it diverges at $\theta = 0, \pi$.

The complete solution $\Theta_{lm}(\theta)\, e^{im\phi} = Y_{lm}(\theta, \phi)$ is the special function called the spherical harmonics. $\Theta_{lm}(\theta)$ is the associated Legendre polynomial.

Like the SHO case we can only list a few solutions:

TABLE 8.1

The first few angular functions $\Theta_{l,m}(\theta)$. The functions with m negative are given by $\Theta_{l,-m} = (-1)^m \Theta_{l,m}$.

	$l = 0$	$l = 1$	$l = 2$
$m = 0$	$\sqrt{1/4\pi}$	$\sqrt{3/4\pi}\cos\theta$	$\sqrt{5/16\pi}\,(3\cos^2\theta - 1)$
$m = 1$		$-\sqrt{3/8\pi}\sin\theta$	$-\sqrt{15/8\pi}\sin\theta\cos\theta$
$m = 2$			$\sqrt{15/32\pi}\sin^2\theta$

Energy levels of hydrogen atoms: to solve for these we need to use

$U(r) = -\frac{ke^2}{r}$ for the radial equation:

$$\frac{r}{R}\frac{d^2}{dr^2}(rR) - l(l+1) - \frac{2M}{\hbar^2}\left[U(r) - E\right] r^2 = 0 \qquad M = m_e \text{ electron's mass}$$

$$\frac{1}{r}\frac{d^2}{dr^2}(rR) - \left[\frac{l(l+1)}{r^2} - \frac{2m_e}{\hbar^2}\left(\frac{ke^2}{r} + E\right)\right]R = 0 \qquad \left(\text{more precisely } M = \frac{m_e m_p}{m_p + m_e}\right)$$

or $$\frac{d^2}{dr^2}(rR) = \frac{2m_e}{\hbar^2}\left(-E - \frac{ke^2}{r} + \frac{\hbar^2 l(l+1)}{2m_e r^2}\right)(rR)$$

We can only quote the solutions here. The energy levels are quantized (labeled by n only & is independent of l!)

$$E_n = -\frac{m_e(ke^2)^2}{2\hbar^2}\frac{1}{n^2} = -\frac{E_R}{n^2} \qquad E_R \simeq 13.6\,\text{eV} \text{ exactly what Bohr had.}$$

Integer n is called the principal quantum number $n > l$

This means for a given n: $\ell = 0, 1, 2, \cdots, n-1$ & $\underbrace{m = -\ell, -\ell+1, \cdots, \ell}_{2\ell+1}$

The degeneracy is $\sum_{\ell=0}^{n-1} (2\ell+1) = n^2$

Wave fcn $\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\phi)$

Bohr hydrogen atom model

Total energy is $E = \frac{1}{2} m_e v^2 - \frac{ke^2}{r}$ but $m\frac{v^2}{r} = \frac{ke^2}{r^2} \Rightarrow m_e v^2 = \frac{ke^2}{r}$

$$= -\frac{ke^2}{2r} = -\frac{1}{2} m_e v^2$$

Bohr assumed "L" $= m_e v r$ is quantized "L" $= m_e v r = n\hbar$

$$v = \frac{n\hbar}{m_e r} \Rightarrow m_e \left(\frac{n\hbar}{m_e r}\right)^2 = \frac{ke^2}{r} \qquad \frac{n^2\hbar^2}{m_e\, r_n} = ke^2 \Rightarrow \frac{1}{r_n} = \frac{m_e k e^2}{\hbar^2 n^2}$$

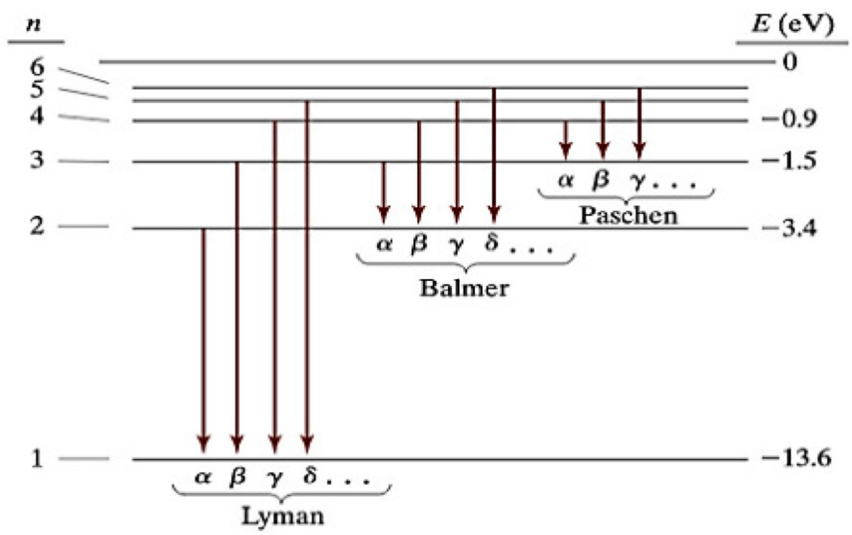
$$\Rightarrow E_n = -\frac{ke^2}{2r_n} = -\frac{m_e (ke^2)^2}{2\hbar^2}\frac{1}{n^2} \qquad a_B = \frac{\hbar^2}{m_e ke^2} \text{ Bohr radius} \qquad = \frac{1}{n^2 a_B}$$

Some the wrong angular momentum quantization leads to correct energy spectrum !! ["n" has nothing to do with $\vec{L}$!!]

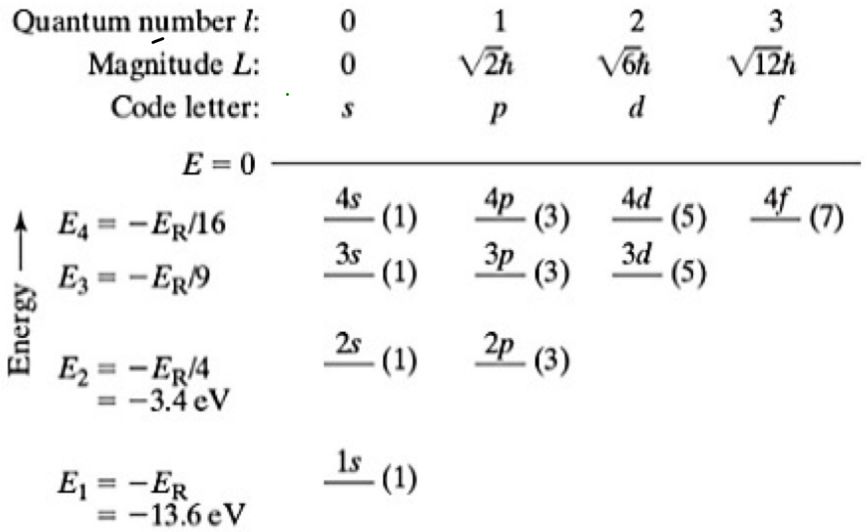
0.0529 nm

n_i $\downarrow$ n_f $\qquad hf = E_{n_i} - E_{n_f} = E_R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

photon emitted as the electron jumps for n_i to n_f



Energy level diagram : this illustrates a few energy levels



$s, p, d,$ and f stood for *sharp*, *principal*, *diffuse*, and *fundamental*.

What do these wave functions look like?

The ground state has $n=1$, $l=0$ & $m=0$ so the radial equation is

$$\frac{d^2}{dr^2}(rR) = \frac{2m_e}{\hbar^2}\left[-\frac{ke^2}{r} + \frac{E_R}{n^2}\right](rR) \quad \text{(let's keep } n\text{)}$$

$$a_B = \frac{\hbar^2}{m_e k e^2} \Rightarrow \frac{d^2}{dr^2}(rR) = \left(\frac{1}{n^2 a_B^2} - \frac{2}{a_B r}\right)(rR)$$

For $n=1$, we can verify that

1s wavefunction: $R_{1s}(r) = A\, e^{-r/a_B}$ is a solution

Prob 8.39. Omit A:

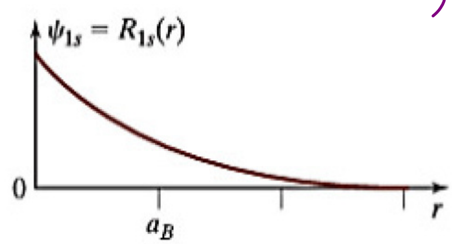
$$\text{l.h.s}: \quad \frac{d^2}{dr^2}(rR) = 2R' + rR''$$

$$R' = -\frac{1}{a_B} e^{-r/a_B} \; ; \; R'' = \frac{1}{a_B^2} e^{-r/a_B}$$

$$\text{l.h.s} = \left(-\frac{2}{a_B} + \frac{r}{a_B^2}\right) e^{-r/a_B}$$

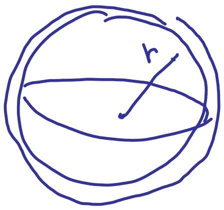
$$\text{r.h.s.} = \left(\frac{1}{a_B^2} - \frac{2}{a_B r}\right) \cdot r\, e^{-r/a_B} = \text{l.h.s}$$

$|\psi|^2$ maximum @ $r=0$ (a property for all s orbitals)



* But for $l \neq 0$, $|\psi(r=0)|^2 = 0$

But at radius r, the area is $4\pi r^2$ for the surface of a sphere

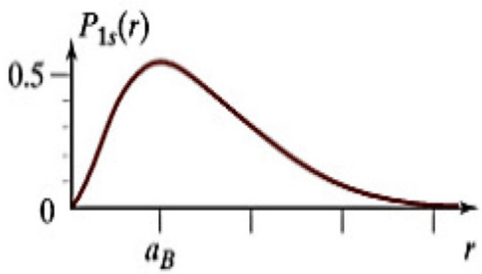


the probability of finding e^- in the thin shell between r & $r+dr$

is $P(r)\,dr = |\psi(r)|^2 \, 4\pi r^2 \, dr$

$\Uparrow$ radial probability density

$$P_{1s}(r) = |A|^2 \, 4\pi r^2 e^{-2r/a_B}$$



Q: where is $P_{1s}(r)$ peaked?

To find this, consider $\dfrac{dP_{1s}(r)}{dr} = 0$

$$\frac{d}{dr}\left(r^2 e^{-2r/a_B}\right) = 0 \qquad 2r\,e^{-2r/a_B} - 2\frac{r^2}{a_B} e^{-2r/a_B} = 0$$

$$\Rightarrow \boxed{r_{peak} = a_B}$$

Example 8.4

Find the constant A in the 1s wave function $R_{1s} = Ae^{-r/a_B}$ and the expectation value of the potential energy for the ground state of hydrogen.

① Use normalization

$$1 = \int_0^\infty P_{1s}(r)\,dr = A^2 \, 4\pi \int_0^\infty r^2 e^{-2r/a_B}\,dr$$

$$= \underbrace{r^2\left(-\frac{a_B}{2} e^{-\frac{2r}{a_B}}\right)}_{=0}\Bigg|_0^\infty - \int 2r\left(-\frac{a_B}{2} e^{-\frac{2r}{a_B}}\right) dr$$

$$= 4\pi A^2 a_B \int_0^\infty r e^{-\frac{2r}{a_B}}\,dr = 4\pi A^2 a_B \left[\underbrace{r\left(-\frac{a_B}{2}\right) e^{-\frac{2r}{a_B}}\Big|_0^\infty}_{=0} - \left(-\frac{a_B}{2}\right)\int e^{-\frac{2r}{a_B}}\,dr \right]$$

$$= 4\pi A^2 \frac{a_B^2}{2} \int_0^\infty e^{-\frac{2r}{a_B}}\,dr = 4\pi A^2 \frac{a_B^2}{2} \cdot \frac{a_B}{2}$$

So. $A^2 = \dfrac{1}{\pi a_B^3} \Rightarrow A = \dfrac{1}{\sqrt{\pi a_B^3}}$

(e)

$$\langle U \rangle = A^2 4\pi \int_0^\infty U(r)\, r^2 e^{-\frac{2r}{a_B}}\, dr \qquad U(r) = -\frac{ke^2}{r}$$

$$= \frac{4\pi}{\pi a_B^3}(-ke^2)\int_0^\infty r\, e^{-\frac{2r}{a_B}}\, dr = -\frac{4ke^2}{a_B^3}\cdot\frac{a_B^2}{4} = -\frac{ke^2}{a_B}$$

The 2s wave function: $\left(E_{2s} = -\frac{E_R}{4} \right)$

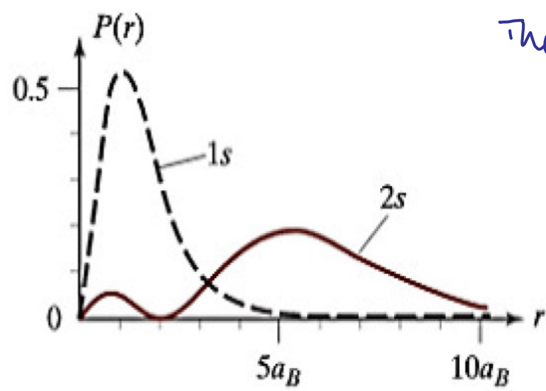
$$\psi_{2s}(r,\theta,\phi) = R_{2s}(r) = A\left(2 - \frac{r}{a_B}\right)e^{-r/2a_B}.$$

[Can verify that this satisfies the radial eq. with $n=2$.]

The radial probability density is

$$P_{2s}(r) = A_{2s}^2 \left(2 - \frac{r}{a_B}\right)^2 e^{-r/a_B} \times 4\pi r^2$$

FIGURE 8.19
The radial distribution $P(r)$ for the $2s$ state (solid curve). The most probable radius is $r \approx 5.2a_B$, with a small secondary maximum at $r \approx 0.76a_B$. For comparison, the dashed curve shows the $1s$ distribution on the same scale. (Vertical axis in units of $1/a_B$.)



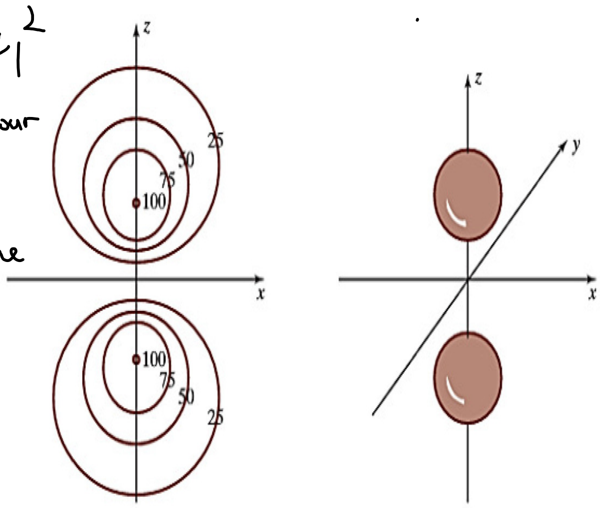
The 2p wave functions

$$\psi_{2,1,0}(r,\theta,\varphi) = R_{2p}(r)\cos\theta = A_{2p}\, e^{-r/2a_B}\, z$$

$$R_{2p}(r) = A_{2p}\, r\, e^{-r/2a_B}$$

$|\psi|^2 = 0$ at $r = 0$.

$|\psi|^2$ Contour on x-z plane



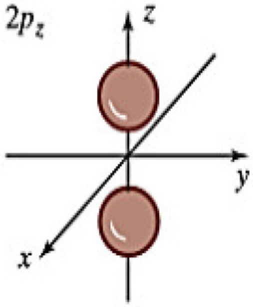
(a) (b)

We also have $2,1,\pm1$, but they are not P_x & P_y orbitals but their linear combinations.

To get P_x & P_y we simply set

$z \to x$ & $z \to y$

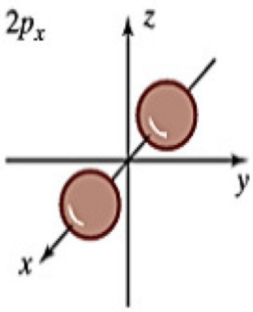
$$\psi_{P_x} = A_{2p}\, e^{-r/2a_B}\, x \; ; \quad \psi_{P_y} = A_{2p}\, e^{-r/2a_B}\, y$$



$|\psi_{2p_z}|^2$ is largest on z-axis at $z = \pm 2a_B$

and zero in the x-y plane.

Probability of finding e^- at a certain distance r from origin



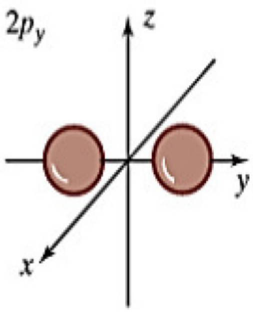
$$P([r, r+dr]) = p(r)\,dr$$

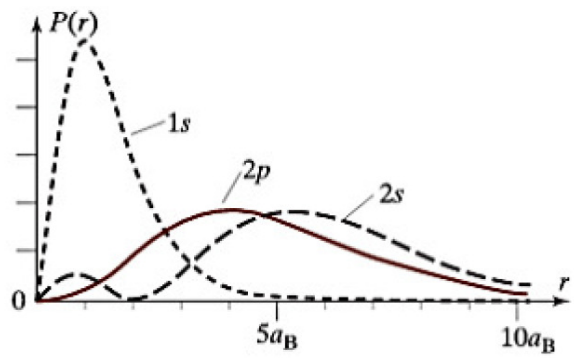
$$p(r)\,dr = 4\pi r^2 \int |\psi(r,\theta,\phi)|^2 \frac{d\Omega}{4\pi}$$

Ω is the solid angle

It is found that

$$P_{2p}(r) = 4\pi r^2 |R_{2p}(r)|^2 = 4\pi A^2 r^4 e^{-r/a_B}$$





The wave function for general state with quantum # n, l, m is

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,\Theta_{lm}(\theta)\,e^{im\phi}$$

TABLE 8.2

The first few radial functions $R_{nl}(r)$ for the hydrogen atom. The variable ρ is an abbreviation for $\rho = r/a_B$ and a stands for a_B.

	$n = 1$	$n = 2$	$n = 3$
$l = 0$	$\frac{2}{\sqrt{a^3}}e^{-\rho}$	$\frac{1}{\sqrt{2a^3}}\left(1 - \frac{1}{2}\rho\right)e^{-\rho/2}$	$\frac{2}{\sqrt{27a^3}}\left(1 - \frac{2}{3}\rho + \frac{2}{27}\rho^2\right)e^{-\rho/3}$
$l = 1$		$\frac{1}{\sqrt{24a^3}}\rho e^{-\rho/2}$	$\frac{8}{27\sqrt{6a^3}}\left(1 - \frac{1}{6}\rho\right)\rho e^{-\rho/3}$
$l = 2$			$\frac{4}{81\sqrt{30a^3}}\rho^2 e^{-\rho/3}$

Shells

Most probable radius for 1s state of hydrogen atom is $r = a_B$

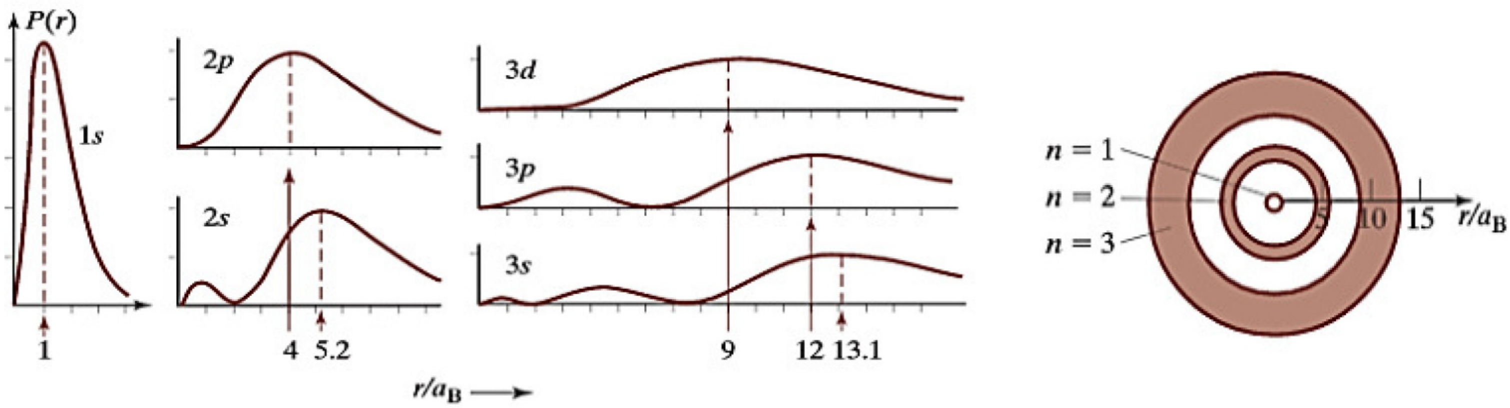
" 2s : $r = 5.2 a_B$

2p : $r = 4 a_B$

3s : $13.1 a_B$

3p : $12 a_B$

3d : $9 a_B$



If we consider how the most probable radii for states, they are close to $n^2 a_B$ (but not exact) (what Bohr concluded for the radii)

Thus we can refer to the structure of hydrogen energy levels to be shells. They are important e.g. for chemistry. [can characterize using energy or spatial distribution.]

Hydrogen-Like Ions [also 5.8]

With the solutions of hydrogen atom, we can easily extend and apply them to hydrogen-like Ions with $U(r) = -\frac{Zke^2}{r}$

① Angular part remains the same

② energy: $E = -\frac{m_e(ke^2)^2}{2\hbar^2}\frac{1}{n^2} = -\frac{E_R}{n} \xrightarrow{ke^2 \to Zke^2} E = -\frac{m_e(Zke^2)^2}{2\hbar^2}\frac{1}{n^2} = -Z^2\frac{E_R}{n}$

③ Spatial extent of wave functions:

$\frac{\hbar^2}{m_eke^2} = a_B \longrightarrow \frac{\hbar^2}{m_eZke^2} = \frac{a_B}{Z}$ $\Longrightarrow$ pull inward by a factor $\frac{1}{Z}$.

$$E_{n_x,n_y} = \underbrace{\frac{\hbar^2\pi^2}{2Ma^2}}_{E_0}(n_x^2+4n_y^2)$$

8.10 •• Consider a particle in a rigid rectangular box with sides a and $b = a/2$. Using the result (8.102) (Problem 8.9), find the lowest six energy levels with their quantum numbers and degeneracies.

$E_{1,1} = 5E_0$

$E_{2,1} = 8E_0$

$E_{3,1} = 13E_0$

$E_{1,2} = 17E_0$

$E_{2,2} = 20E_0 = E_{4,1}$

$E_{3,2} = 25E_0$

$E_{5,1} = 29E_0$

8.15 ••• Show that the allowed energies of a mass M confined in a three-dimensional rectangular rigid box with sides $a, b,$ and c are

$$E = \frac{\hbar^2\pi^2}{2M}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right) \quad (8.103)$$

where the three quantum numbers n_x, n_y, n_z are any three positive integers $(1, 2, 3, \cdots)$. [*Hint:* Use separation of variables, and seek a solution of the form $\psi = X(x)Y(y)Z(z)$. Note that by setting $a = b = c$, one obtains the cubical box of Example 8.2.]

Similar one (2D) in HW 7

$$\frac{\hbar^2\pi^2}{2ma^2}(n_x^2+n_y^2)$$

Harmonic oscillator

1D: $\frac{k}{2}x^2 \rightarrow E_n = \underline{(n+\frac{1}{2})\hbar\omega}$

2D SHO $\frac{k}{2}(x^2+y^2) \rightarrow E_{n_x,n_y} = (n_x+n_y+1)\hbar\omega$

$\frac{1}{2}\hbar\omega_x + \frac{1}{2}\hbar\omega_y$

8.22 •• Substitute the separated form $\psi = R(r)\Theta(\theta)\Phi(\phi)$ into the Schrödinger equation (8.49). **(a)** Show that if you multiply through by $r^2\sin^2\theta/(R\Theta\Phi)$ and rearrange, you get an equation of the form $\Phi''/\Phi =$ (function of r and θ). Explain clearly why each side of this equation must be a constant, which we can call $-m^2$. **(b)** Show that the resulting equation, (function of r and θ) $=-m^2$, can be put in the form

$$\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{m^2}{\sin^2\theta} = \text{(function of } r\text{)}$$

Explain (again) why each side of this equation must be a constant, which we can call $-k$. Derive the r and θ equations (8.54) and (8.53).

already did earlier in lecture.

8.33 ••• The normalization condition for a three-dimensional wave function is $\int |\psi|^2 dV = 1$. **(a)** Show that in spherical polar coordinates, the element of volume is $dV = r^2\, dr \sin\theta\, d\theta\, d\phi$. [*Hint:* Think about the infinitesimal volume between r and $r + dr$, between θ and $\theta + d\theta$, and between ϕ and $\phi + d\phi$.] **(b)** Show that if $\psi = R(r)Y(\theta, \phi)$, the normalization integral is the product of two terms

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

$|\psi|^2 = |R(r)|^2 |Y(\theta,\phi)|^2$

$1 = \int |\psi|^2 dV$

$|e^{im\phi}| = 1$

$$1 = \int |\psi|^2 dV = \left(\int_0^\infty |R(r)|^2 r^2\, dr \right) \times$$

$$1 = \left(\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi |Y(\theta, \phi)|^2 \right) = 1$$

(c) It is usually convenient to normalize the functions $R(r)$ and $Y(\theta, \phi)$ separately, so that each of the factors in this middle expression is equal to 1. Verify that all of the spherical harmonics $Y_{lm}(\theta, \phi)$ with $l = 0$ or 1 do satisfy

$$\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi |Y_{lm}(\theta, \phi)|^2 = 1$$

The required spherical harmonics are defined in (8.69) and Table 8.1.

8.29 •• Write down the θ equation (8.65) for the special case that $l = m = 0$. **(a)** Verify that Θ = constant is a solution. **(b)** Verify that a second solution is $\Theta = \ln[(1 + \cos\theta)/(1 - \cos\theta)]$, and show that this is infinite when $\theta = 0$ or π (and hence is unacceptable). **(c)** Since the θ equation is a second-order differential equation, any solution must be a linear combination of these two. Write down the general solution, and prove that the only acceptable solution is Θ = constant.

(a) did this already
(b)
(c)

8.45 ••• Write down the radial equation (8.72) for the case that $n = 2$ and $l = 1$. Put in the value $-E_R/4$ for the energy and use the known expressions for a_B and E_R to eliminate all dimensional constants except a_B [as was done in (8.80)]. Verify that $R_{2p} = Are^{-r/2a_B}$ is a solution, and use the normalization condition (8.86) with $P_{2p} = 4\pi r^2 |R_{2p}|^2$ to prove that $A = 1/(4\sqrt{6\pi a_B^{\,5}})$.

$a_B = \dfrac{\hbar^2}{m_e k e^2}$;

$E_R = \dfrac{m_e (ke^2)^2}{2\hbar^2} = \dfrac{\hbar^2}{2 m_e a_B^2}$

$$\frac{d^2}{dr^2}(rR) = \frac{2m_e}{\hbar^2}\left(-E - \frac{ke^2}{r} + \frac{\hbar^2 l(l+1)}{2m_e r^2} \right)(rR)$$

1. Omit overall factor A :

$$\frac{d^2}{dr^2}\left(r \cdot r e^{-r/2a_B}\right) \overset{?}{=} \frac{2m_e}{\hbar^2}\left(\frac{E_R}{4} - \frac{ke^2}{r} + \frac{\hbar^2 \cdot 2}{2m_e r^2}\right)\left(r\, r\, e^{-r/2a_B}\right)$$

$$r.h.s = \left(\frac{1}{4a_B^2} - \frac{2}{a_B}\frac{1}{r} + \frac{2}{r^2}\right)\left(r^2 e^{-r/2a_B}\right)$$

l.h.s :

$$\frac{d}{dr}\left(r^2 e^{-r/2a_B}\right) = 2r e^{-r/2a_B} - \frac{r^2}{2a_B} e^{-\frac{r}{2a_B}}$$

$$l.h.s = 2e^{-r/2a_B} - 2\frac{r}{a_B} e^{-r/2a_B} + \frac{r^2}{4a_B^2} e^{-r/2a_B} = r.h.s.$$

$$1 = \int_0^\infty dr\, P_{2p} = A^2 4\pi \underbrace{\int_0^\infty dr\, r^2 r^2 e^{-r/a_B}}_{\frac{d^4}{d\lambda^4}\frac{1}{\lambda} \Rightarrow 4!\,\lambda^{-5}} = 4\pi A^2 \cdot \underbrace{a_B^5 \cdot 4!} \Rightarrow A = \left(\frac{1}{96\pi a_B^5}\right)^{1/2}$$