Problems:

<div align="center">7.8, 7.5, 7.7 **Graded**</div>

1. Starting with $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$ substitute into the Schrödinger equation and show (using the technique of separation of variables) that R satisfies

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{C}{2mr^2} + V(r) \right] R = ER(r) \tag{1}$$

where C is a constant. The equation for $Y(\theta, \phi)$ is

$$\mathbb{L}^2 Y(\theta, \phi) = CY(\theta, \phi) \tag{2}$$

Only for certain values of the constants E and C will the solutions be finite. In particular it turns out that $C = \ell(\ell+1)\hbar^2$ with ℓ an integer.

2. The book writes the radial schrodinger equation for $R_{nl}(r)$ as

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R_{nl}}{\partial r} \right) + \frac{\ell(\ell+1)\hbar^2 R_{nl}}{2mr^2} \right] = E_{nl} R_{nl}(r) \tag{3}$$

Show that the equation for $u_{nl}(r) \equiv \sqrt{4\pi} \, r R_{nl}$ is given by Eq. (36). Show that the $2p$ wave functions of the hydrogen atom satisfy the radial Schrödinger equation.

3. Show that the minimum of the effective potential of the radial shrödinger equation occurs at $r = \ell(\ell+1)a_o$

4. **Graded** Consider the differences between ψ_{210} and ψ_{200}:

   (a) Sketch the effective radial potential for these two wave functions

   (b) Sketch radial wavefunctions rR_{nl} associated with ψ_{210} and ψ_{200} and corresponding radial probability density $\mathscr{P}(r)$. Despite the fact that these states have the same energy, their radial wave fuctions are qualitatively different, explain.

   (c) Determine the most likely radial position for the electron for the ψ_{200} state. Be sure to look carefully at your graphs in part (b) – see also Fig 7.5 of book. (Ans: $r = (3 + \sqrt{5})a_o \simeq 5.236a_o$. Hint there are two maxima at $r = (3 \pm \sqrt{5})a_o$)

5. List all the levels associated of the second excited state of hydrogen. What is the energy of these states, what are the angular momentum squared of these states, what are the z-component of angular momentum of these states.

<div align="center">1</div>

2D Shrödinger Equation

1. In two dimensions the Schrödinger equations reads

$$\left[\frac{\mathbb{P}_x^2}{2m} + \frac{\mathbb{P}_y^2}{2m} + V(x,y)\right]\Psi(x,y) = E\Psi(x,y) \tag{4}$$

$$\left[\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x,y)\right]\Psi(x,y) = E\Psi(x,y) \tag{5}$$

2. For the particle in the two dimensional box the potential is

$$V = \begin{cases} 0 & \text{inside box } -L/2 < x, y < L/2 \\ \infty & \text{outside box} \end{cases} \tag{6}$$

We solved this equation using separation of variables making an ansatz $\Psi(x,y) = \mathsf{X}(x)\mathsf{Y}(y)$ and solving for the functions X and Y

3. We will discuss a square box $L_x = L_y = L$ but you should be able to generalize this to a rectangular box and also to three dimensions

   (a) The wave functions are described by two quantum numbers n_x, n_y and are

   $$\Psi_{n_x,n_y}(x,y) = \mathsf{X}_{n_x}(x)\mathsf{Y}_{n_y}(y) \tag{7}$$

   with

   $$n_x = 1, 2, 3, \ldots \qquad \text{and} \qquad n_y = 1, 2, 3, \ldots \tag{8}$$

   Where

   $$\mathsf{X}_{n_x}(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{n_x\pi x}{L}\right) & n_x = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n_x\pi x}{L}\right) & n_x = 2, 4, 6, \ldots \end{cases} \tag{9}$$

   and similarly

   $$\mathsf{Y}_{n_y}(y) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{n_y\pi y}{L}\right) & n_y = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n_y\pi y}{L}\right) & n_y = 2, 4, 6, \ldots \end{cases} \tag{10}$$

   (b) The wave functions $\mathsf{X}(x)$ and $\mathsf{Y}(y)$ satisfy the one dimensional Schrödinger equation.

   $$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\mathsf{X}(x) = \epsilon_x\mathsf{X} \tag{11}$$

   (c) The Energies are a sum of the kinetic energies in the x and y directions

   $$E_{n_x,n_y} = \epsilon_x + \epsilon_y \tag{12}$$

   $$= \frac{\hbar^2\pi^2}{2ML^2}n_x^2 + \frac{\hbar^2\pi^2}{2ML^2}n_y^2 \tag{13}$$

   (d) Some wave functions can have the same energy which is known as a degeneracy. For instance the following two states are degenerate for a square box

   $$E_{21} = E_{12} = \frac{\hbar^2\pi^2}{2ML^2}5 \tag{14}$$

   This is a consequence of the fact that the x direction is no different from the y. There is a symmety in the problem

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Particle in a Spherical Potential

1. For a particle moving in a Spherically symmetric potiential all the forces are in the radial direction

$$F(r) = -\frac{\partial V(r)}{\partial r}\hat{r} \tag{15}$$

   We are generally considering an electron moving in the Coulomb field of a proton. In this case the potential and forces are the familiar

$$V(r) = \frac{-e^2}{4\pi\epsilon_o}\frac{1}{r} \qquad F(r) = -\frac{e^2}{4\pi\epsilon_o r^2}\hat{r} \tag{16}$$

   but we will leave $V(r)$ general for discussion.

2. The kinetic energy operator is

$$\frac{-\hbar^2}{2m}\nabla^2 \equiv \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{17}$$

$$= \frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\right) \tag{18}$$

$$= \frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\mathbb{L}^2}{2mr^2} \tag{19}$$

   Here we have defined the angular momentum squared operator

$$\mathbb{L}^2 = -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{20}$$

3. The Schrödinger equation reads

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V(r)\right]\psi_{nlm}(r,\theta,\phi) = E_{nl}\psi_{nlm}(r,\theta,\phi) \tag{21}$$

   The wave functions depend on the quantum numbers nlm but it turns out that the energies do not depend on m.

4. For *any* radially symmetric potential the wave function is in general written as a product of radial wave function $R_{nl}(r)$ and angular wave functions Θ and Φ

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\underbrace{\Theta_{lm}(\theta)\Phi_m(\phi)}_{\equiv Y_{lm}(\theta,\phi)} \tag{22}$$

   Here th labels n, l and m are the quantum numbers. One for each dimension r,θ,ϕ. Note the labels: for instace $R_{nl}(r)$ depends only on n and l but not m The prodct of Θ and Φ is known as a *spherical harmonic* $Y_{lm}(\theta,\phi) \equiv \Theta_{lm}(\theta)\Phi_m(\phi)$. For $\ell = 0$ there is no angular dependence and $Y_{00} = 1$ and $\Theta_{lm} = 1$.

5. Substituting the wave function of $\psi = R(r)Y(\theta,\phi)$ into the shrodinger equation we find an equation for R and an equation for Y.

   (a) The equation for R is the radial schrodinger equation is discussed in the next section

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right]R_{nl} = E_{nl}R_{nl}(r) \tag{23}$$

   The solutions R_{nl} depend on the potential $V(r)$

   (b) The equation for $Y_{lm}(\theta,\phi)$ is discussed below

$$\mathbb{L}^2 Y_{lm}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{lm}(\theta,\phi) \tag{24}$$

   Only for certain values of the constants E and $\ell(\ell+1)\hbar^2$ will the solutions be bounded. In particular it turns out that ℓ must be an integer. The functions $Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$ are shown in table (53). The angular piece is valid for all spherically symmetric potentials, while the radial piece is specific to hydrogen.

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6. In general the wave functions are characterized by the three quantum numers

   (a) The *principle* quantum number

   $$n = 1, 2, 3, 4 \ldots \tag{25}$$

   labels the total number of excitations of the wave function More precisely $n - 1$ is the total number of excitations in either the radial or angular directions.

   - **Note:** For a general radial potential the energy of the wave depends on wether the excitation is in the angular or radial direction. Thus the energy is a function of n and ℓ, $E_{n\ell}$. For the specific case of hydrogen where $V(r) \propto 1/r$ the energy only depends on n due to a peculiarity of the Coulomb Law, where $E_{n\ell} = -13.6/n^2$

   (b) The angular momentum quantum number ℓ

   $$\ell = 0, 1, \ldots n - 1 \tag{26}$$

   counts the total number of angular excitations of the wave, which must be less than the total, $n - 1$. These wave functions have definite angular momentum

   $$\overline{\mathbb{L}^2} = \ell(\ell + 1)\hbar^2. \tag{27}$$

   $\ell = 0, 1, 2, 3, 4 \ldots$ also called by the names "sharp, principle, diffuse"

   $$\ell = s, p, d, f, g \tag{28}$$

   i.e. an "s-wave" is another name for the $\ell = 0$ wave function.

   - **Note:** The number of radial excitations is $(n - 1) - \ell$

   (c) And a finally "magnetic" quantum number. $|m|$ is the number of azimuthal angular excitations around the z axis. with

   $$m = 0, \pm 1, \pm 2, \pm 3 \ldots \pm \ell \tag{29}$$

   Clearly the number of azimuthal excitations should be less than ℓ. The sign indicates wether the angular excitation is counter-clocwise $m > 0$ (i.e. if you use the right hand rule your thumb points up) or clockwise $m < 0$ These wave functions have definite z component of angular moemntum

   $$\overline{\mathbb{L}_z} = m\hbar \, Y_{\ell m} \tag{30}$$

   which can be positive or negative.

7. Examples:

   (a) Thus for $n = 2$ (the first excited state) we the following four states

   $$\underbrace{(n = 2, \ell = 0, m = 0)}_{\text{s-wave, 2s}} \qquad \underbrace{(n = 2, \ell = 1, m = -1) \qquad (n = 2, \ell = 1, m = 0) \qquad (n = 2, \ell = 1, m = +1)}_{\text{p-wave, 2p}}$$

   $$\tag{31}$$

   For the hydrogen atom these states are listed in Eq. (53)

   (b) When we refer to the $3d$ state, we mean $n = 3$ and $\ell = 2$ and $m = -2, -1, 0, 1, 2$

Radial Part of Schrödinger Equation

1. For $\ell = 0$ $m = 0$ the wave function is independent of angle $\Theta_{00} = \Phi_0 = 1$.

$$\Psi_{n00} = R_{n0}(r) \tag{32}$$

2. The probability dP is

$$\mathrm{dP} = |\Psi|^2\, dV = |R_{nl}(r)|^2 4\pi r^2 dr = \mathscr{P}(r) dr \tag{33}$$

where the $4\pi r^2 dr$ is the volume of a spherical shell. Thus:

(a) The probability to find a particle *per volume* is $|\Psi|^2$

(b) The probability to find a particel *per unit radius* is:

$$\mathscr{P}(r) = |R_{nl}|^2 4\pi r^2 = |u_{nl}(r)|^2 \tag{34}$$

where we have defined the $u_{nl}(r) = \sqrt{4\pi r^2} R_{nl}(r)$

(c) The functions are normalized so that

$$\int \mathrm{dP} = \int_0^\infty |R_{nl}(r)|^2 4\pi r^2 dr = \int_0^\infty |u_{nl}(r)|^2 dr = 1 \tag{35}$$

3. As in the previous item, it is useful to define the "radial wave function" u_{nl}

$$u_{nl}(r) \equiv \sqrt{4\pi}\, r R_{nl}(r)$$

This is useful because then $\mathscr{P}(r) = |u_{nl}(r)|^2$ as described above. If the wave function of the form given in Eq. (22), then the radial Schrödinger equation for R (Eq. (23)) reduces to the the radial Schrödinger equation for u_{nl}

$$\left[\underbrace{\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial r^2}}_{\text{radial KE}} + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2mr^2}}_{\text{angular KE}} + V(r) \right] u_{n\ell} = E_{nl} u_{nl} \tag{36}$$

(a) For $\ell = 0$ (no angular momentum) this reduces to a $1D$ shrodinger equation in the potential $V(r)$.

(b) For $\ell \neq 0$ there is an extra "potential" which represents the kinetic energy in the agular direction, i.e.

$$V_{\text{eff}}(r) = V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} \tag{37}$$

By considering the motion of a particle in a circle you should be able to show classically that

$$KE = \underbrace{\frac{1}{2}mv_r^2}_{\text{radial KE}} + \underbrace{\frac{L^2}{2mr^2}}_{\text{angular KE}} \tag{38}$$

where $L = mv_\perp r$ is the angular momentum. For a wave function with agular quantum number ℓ the angular momentum $\overline{L^2} = \ell(\ell+1)\hbar^2$ as discussed in Eq. (27). Thus the form of this extra potential is understandable.

(c) You should be able to graph the effecitve potential and qualitatively sketch the wave function as in one dimension.

(d) To understand the effect of this this extra potential, we note first that the "centripetal force" for a classical particle moving in a circle is

$$F_C = m\frac{v^2}{r}\hat{\boldsymbol{r}} = \frac{L^2}{mr^3}\hat{\boldsymbol{r}} \tag{39}$$

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where $L = mvr$ is the angular momentum. For a state with agular quantum number the angular momentum $\overline{\mathbb{L}^2} = \ell(\ell+1)\hbar^2$ as discussed near Eq. (27). Then we note that the "force" due to this extra potential

$$F_C = -\frac{\partial}{\partial r}\frac{\ell(\ell+1)\hbar^2}{2mr^2}\,\hat{\boldsymbol{r}} = \frac{\overline{\mathbb{L}^2}}{mr^3}\,\hat{\boldsymbol{r}} \tag{40}$$

Thus the effect of this extra term is to provide the "centripetal force". Classically there is no real "centripetal force". It just summarizes the effect of the circular motion on the radial direction. Similarly there is no extra potential really, it is just the effect of the angular kinetic energy on the radial dynamics.

4. We can average different quantities

$$\overline{PE} = \int_0^\infty \frac{-e^2}{4\pi\epsilon_o r}\,\mathscr{P}(r)dr \tag{41}$$

and

$$\bar{r} = \int_0^\infty r\,\mathscr{P}(r)dr \tag{42}$$

The variance in the radius is

$$(\Delta r)^2 \equiv \overline{r^2} - \bar{r}^2 \tag{43}$$

5. The average kinetic energy is

$$\overline{KE} = \int_0^\infty u_{nl}^* \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} \right] u_{nl}\,dr \tag{44}$$

6. You should be able to verify that this or that functions satisfies the radial Schrödinger equation. You should be able to describe the qualitative features

Angular Part of the Schrodinger Equation:

1. The wave functions have definite squared angular momentum labeled by the orbital quantum number ℓ and m

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi) \tag{45}$$

so that

$$\mathbb{L}^2 Y_{lm} = \ell(\ell+1)\hbar^2 \, Y_{lm} \tag{46}$$

The magnetic quantum number m records the angular momentum about the z-axis.

$$\mathbb{L}_z Y_{lm} = m\hbar \, Y_{lm} \tag{47}$$

where the angular momentum squared operator and are

$$\mathbb{L}^2 = -\hbar^2 \left(\frac{1}{\sin(\theta)} \frac{\partial}{\partial\theta} \sin(\theta) \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) \tag{48}$$

$$\mathbb{L}_z = -i\hbar \frac{\partial}{\partial\phi} \tag{49}$$

ℓ	m	$\Phi_m(\phi)$	$\Theta_{lm}(\theta)$
0	0	1	1
1	0	1	$\sqrt{3}\cos(\theta)$
1	± 1	$e^{\pm i\phi}$	$\sqrt{\frac{3}{2}}\sin(\theta)$
2	0	1	$\frac{\sqrt{5}}{4}(3\cos(2\theta)+1)$
2	± 1	$e^{\pm i\phi}$	$\sqrt{\frac{15}{2}}\sin(\theta)\cos(\theta)$
2	± 2	$e^{\pm i2\phi}$	$\frac{1}{2}\sqrt{\frac{15}{2}}\sin^2(\theta)$

$$\tag{50}$$

Hydrogen Atom

- For the special case of the hydrogen atom the potential $V(r)$ is just the Coulomb potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_o r} \tag{51}$$

- The energies are

$$E_{n\ell} = -\frac{\hbar^2}{2ma_0^2}\frac{Z^2}{n^2} = -\frac{1}{2}\frac{e^2}{4\pi\epsilon_o a_0}\frac{Z^2}{n^2} \tag{52}$$

We note that the fact that the energies are independent of ℓ for the hydrogen atom is special to the $1/r$ potential.

- The lowest order wave functions are

n	ℓ	m		$\Phi_m(\phi)$	$\Theta_{lm}(\theta)$	$R_{nl}(r)$	Ψ_{nlm}
1	0	0	$1s$	1	1	$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$	$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$
2	0	0	$2s$	1	1	$\frac{1}{\sqrt{32\pi a_o^3}}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$	$\frac{1}{\sqrt{32\pi a_o^3}}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$
2	1	0	$2p$	1	$\sqrt{3}\cos(\theta)$	$\frac{1}{\sqrt{96\pi a_o^3}}\frac{r}{a_o}e^{-r/2a_o}$	$\frac{1}{\sqrt{32\pi a_o^3}}\frac{r}{a_o}e^{-r/2a_o}\cos(\theta)$
2	1	±1	$2p$	$e^{\pm i\phi}$	$\sqrt{\frac{3}{2}}\sin(\theta)$	$\frac{1}{\sqrt{96\pi a_o^3}}\frac{r}{a_o}e^{-r/2a_o}$	$\frac{1}{\sqrt{64\pi a_o^3}}\frac{r}{a_o}e^{-r/2a_o}\sin(\theta)e^{\pm i\phi}$

$$\tag{53}$$

- An integral which comes up a lot is

$$\int_0^\infty dx\, x^n e^{-x} = n! \tag{54}$$

- For $n=3$ we will quote the R_{nl} only. For the necessary table of Θ_{lm} and Φ_m see Eq. 50. Here

$$\rho \equiv \frac{2r}{3a_o} \tag{55}$$

n	ℓ	$R_{n\ell}$
3	0	$\sqrt{\frac{40}{(4\pi)6!}}\left(\frac{2}{3a_o}\right)^{3/2}\frac{1}{2}\left(6-6\rho+\rho^2\right)e^{-\rho/2}$
3	1	$\sqrt{\frac{5}{(4\pi)6!}}\left(\frac{2}{3a_o}\right)^{3/2}(4-\rho)\,\rho\, e^{-\rho/2}$
3	2	$\sqrt{\frac{1}{(4\pi)6!}}\left(\frac{2}{3a_o}\right)^{3/2}\rho^2\, e^{-\rho/2}$

$$\tag{56}$$