

Problems:

1. **Periodic Table.** What is the electronic structure of Ne, $Z = 10$. Make an educated guess about its chemical reactivity. What is the electronic structure of Oxygen $Z = 8$. What is the electronic structure of iron, $Z = 26$. Explain why there is 10 boxes in the middle of the periodic table.
2. V_{eff} **practice:** In a strange parallel universe the attraction between the electron and proton is not the Coulomb Law but is

$$V(r) = \frac{1}{2}kr^2$$

On the same graph, sketch the effective potential in this case for $\ell = 0$ and $\ell = 1$ and $\ell = 2$.

3. **Inflection points and classical solutions:** Consider the $3p$ state of hydrogen. Graph the effective potential in this case. Sketch the $3p$ radial wave function. Determine the inflection points of the radial wave function u_{nl} – the table of wave functions given in class is useful. (Ans. $1.06a_0, 6a_0, 16.93a_0$)
4. **Classical orbits:** Consider the classical orbits corresponding to the $3p$ orbits, i.e. those orbits with $L^2 = \ell(\ell + 1)\hbar^2$ and energy $E = -[\hbar^2/(2ma_0^2)]1/n^2$. What is the maximum and minimum velocities of the electron in units of the speed of light, and what is the maximum radial velocity of the orbit. (Hint: Use the results of the previous that the classical turning points are at $r = 3(3 - \sqrt{7})a_0 \simeq 1.06a_0$ and $r = 3(3 + \sqrt{7})a_0 \simeq 16.93a_0$. Also use the result that the minimum of the effective potential is at $r = \ell(\ell + 1)a_0$ as we showed previously.)

Extra Practice

1. **Averages of PE, Angular KE, KE,:** Determine the average angular kinetic energy, and the average potential energy, and the average KE, of the $2p$ state of hydrogen. (Answers: ave PE = $-27.2 \text{ eV}/4$, ave angular KE = $13.6 \text{ eV}/6$, and finally we have:

$$\text{ave KE} = E - \bar{V} = -13.6 \text{ eV}/4 + 27.2 \text{ eV}/4$$

As a challenge compute the average radial KE directly from Eq. (45) and show that

$$\text{ave KE} = \text{ave radial KE} + \text{ave angular KE}$$

2. **Average and variance of radius** Determine the variance in radius of the $2p$ state.
3. **Verify solution:** Show that the $2p$ wave function satisfies the radial Schrödinger equation
4. **Sketch radial wave fncs:** Sketch the $3s, 3p, 3d$ radial wave functions. Why are the wave functions qualitatively different.
5. **Wave function-Taxonomy:** What is the total degeneracy of $n = 3$ states. List the states. What is the squared angular momentum and the z-component of the angular momentum for each of these states.

2D Schrödinger Equation

1. In two dimensions the Schrödinger equation reads

$$\left[\frac{\mathbb{P}_x^2}{2m} + \frac{\mathbb{P}_y^2}{2m} + V(x, y) \right] \Psi(x, y) = E\Psi(x, y) \quad (1)$$

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

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

$$V = \begin{cases} 0 & \text{inside box } -L/2 < x, y < L/2 \\ \infty & \text{outside box} \end{cases} \quad (3)$$

We solved this equation using separation of variables making an ansatz $\Psi(x, y) = X(x)Y(y)$ 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

$$\Psi_{n_x, n_y}(x, y) = X_{n_x}(x)Y_{n_y}(y) \quad (4)$$

with

$$n_x = 1, 2, 3, \dots \quad \text{and} \quad n_y = 1, 2, 3, \dots \quad (5)$$

Where

$$X_{n_x}(x) = \begin{cases} \sqrt{\frac{2}{L}} \cos\left(\frac{n_x \pi x}{L}\right) & n_x = 1, 3, 5, \dots \\ \sqrt{\frac{2}{L}} \sin\left(\frac{n_x \pi x}{L}\right) & n_x = 2, 4, 6, \dots \end{cases} \quad (6)$$

and similarly

$$Y_{n_y}(y) = \begin{cases} \sqrt{\frac{2}{L}} \cos\left(\frac{n_y \pi y}{L}\right) & n_y = 1, 3, 5, \dots \\ \sqrt{\frac{2}{L}} \sin\left(\frac{n_y \pi y}{L}\right) & n_y = 2, 4, 6, \dots \end{cases} \quad (7)$$

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

$$\left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right] X(x) = \epsilon_x X \quad (8)$$

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

$$\begin{aligned} E_{n_x, n_y} &= \epsilon_x + \epsilon_y & (9) \\ &= \frac{\hbar^2 \pi^2}{2ML^2} n_x^2 + \frac{\hbar^2 \pi^2}{2ML^2} n_y^2 & (10) \end{aligned}$$

(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

$$E_{21} = E_{12} = \frac{\hbar^2 \pi^2}{2ML^2} 5 \quad (11)$$

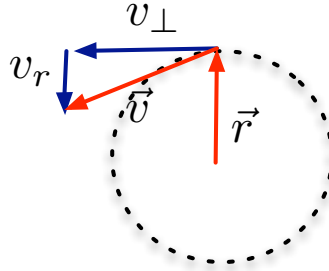
This is a consequence of the fact that the x direction is no different from the y . There is a symmetry in the problem

Particle in a Spherical Potential (Classical)

1. Energy is constant

$$\frac{1}{2}mv^2 + V(r) = E \quad (12)$$

We note that if \mathbf{v} is broken up into radial and perpendicular components as shown below (so that $KE = 1/2 mv_r^2 + 1/2 mv_\perp^2$),



we use that $1/2 mv_\perp^2 = L^2/(2mr^2)$ yielding

$$\frac{1}{2}mv_r^2 + \underbrace{\frac{L^2}{2mr^2}}_{\equiv V_{\text{eff}}(r)} + V(r) = E \quad (13)$$

where we have defined the effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{L^2}{2mr^2} \quad (14)$$

- (a) $E - V$ determines the kinetic energy
- (b) $E - V_{\text{eff}}(r)$ determines the radial KE or $1/2 mv_r^2$
- (c) V_{eff} depends on the angular momentum of the orbit

2. The angular momentum is a constant. This is because the force points along \mathbf{r} and hence the torque $\boldsymbol{\tau} = \mathbf{r} \times \mathbf{F} = 0$. Thus for a classical orbit

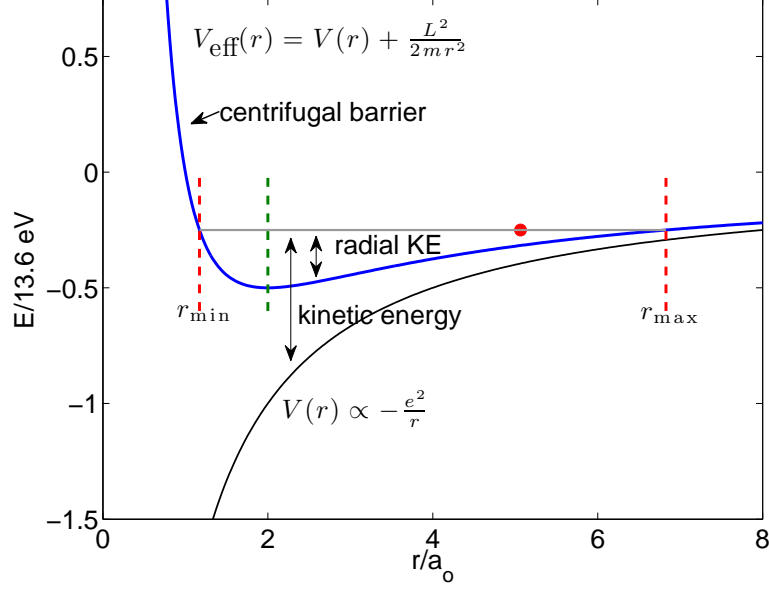
$$L = mrv_\perp = mr^2\omega \quad (15)$$

is constant. You should also remember that v_\perp can be related to the angular velocity

$$v_\perp = r\omega \quad \text{where} \quad \omega = \frac{d\theta}{dt}$$

For small radii ω is large, while for large radii ω is small

3. You should understand this picture based on lecture which summarizes these points



The classical turning points happen when $E = V_{\text{eff}}$

Particle in a Spherical Potential (Quantum)

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

$$F(r) = -\frac{\partial V(r)}{\partial r} \hat{r} \quad (16)$$

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

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r} \quad F(r) = -\frac{e^2}{4\pi\epsilon_0 r^2} \hat{r} \quad (17)$$

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

2. The kinetic energy operator is

$$\frac{-\hbar^2}{2m} \nabla^2 \equiv \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad (18)$$

$$= \frac{-\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \right) \quad (19)$$

$$= \frac{-\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\mathbb{L}^2}{2mr^2} \quad (20)$$

Here we have defined the angular momentum squared operator

$$\mathbb{L}^2 = -\hbar^2 \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (21)$$

3. The Schrödinger equation reads

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_{nlm}(r, \theta, \phi) = E_{nl} \psi_{nlm}(r, \theta, \phi) \quad (22)$$

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

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \underbrace{\Theta_{lm}(\theta)\Phi_m(\phi)}_{\equiv Y_{lm}(\theta, \phi)} \quad (23)$$

Here the labels n , l and m are the quantum numbers. One for each dimension r, θ, ϕ . Note the labels: for instance $R_{nl}(r)$ depends only on n and l but not m . The product 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 $\Theta_{l0} = 1$.

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

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

$$\left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r) \right] R_{nl} = E_{nl} R_{nl}(r) \quad (24)$$

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

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

$$\mathbb{L}^2 Y_{lm}(\theta, \phi) = \ell(\ell+1)\hbar^2 Y_{lm}(\theta, \phi) \quad (25)$$

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 (54). The angular piece is valid for all spherically symmetric potentials, while the radial piece is specific to hydrogen.

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

- (a) The *principle* quantum number

$$n = 1, 2, 3, 4, \dots \quad (26)$$

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 whether 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

$$\ell = 0, 1, \dots, n-1 \quad (27)$$

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

$$\overline{\mathbb{L}^2} = \ell(\ell+1)\hbar^2. \quad (28)$$

$\ell = 0, 1, 2, 3, 4, \dots$ also called by the names “sharp, principle, diffuse”

$$\ell = s, p, d, f, g \quad (29)$$

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

$$m = 0, \pm 1, \pm 2, \pm 3, \dots, \pm \ell \quad (30)$$

Clearly the number of azimuthal excitations should be less than ℓ . The sign indicates whether the angular excitation is counter-clockwise $m > 0$ (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 momentum

$$\overline{\mathbb{L}_z} = m\hbar Y_{lm} \quad (31)$$

which can be positive or negative.

7. Examples:

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

$$\underbrace{(n = 2, \ell = 0, m = 0)}_{\text{s-wave, 2s}} \quad \underbrace{(n = 2, \ell = 1, m = -1) \quad (n = 2, \ell = 1, m = 0) \quad (n = 2, \ell = 1, m = +1)}_{\text{p-wave, 2p}} \quad (32)$$

For the hydrogen atom these states are listed in Eq. (54)

(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 $\Theta_{00} = \Phi_0 = 1$.

$$\Psi_{n00} = R_{n0}(r) \quad (33)$$

2. The probability $d\mathcal{P}$ is

$$d\mathcal{P} = |\Psi|^2 dV = |R_{nl}(r)|^2 4\pi r^2 dr = P(r) dr \quad (34)$$

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 particle *per unit radius* is:

$$P(r) = |R_{nl}|^2 4\pi r^2 = |u_{nl}(r)|^2 \quad (35)$$

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

- (c) The functions are normalized so that

$$\int d\mathcal{P} = \int_0^\infty |R_{nl}(r)|^2 4\pi r^2 dr = \int_0^\infty |u_{nl}(r)|^2 dr = 1 \quad (36)$$

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 $P(r) = |u_{nl}(r)|^2$ as described above. If the wave function of the form given in Eq. (23), then the radial Schrödinger equation for R (Eq. (24)) reduces to the the radial Schrödinger equation for u_{nl}

$$\left[\underbrace{\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial r^2}}_{\text{radial KE}} + \underbrace{\frac{\ell(\ell+1)\hbar^2}{2mr^2}}_{\text{angular KE}} + V(r) \right] u_{nl} = E_{nl} u_{nl} \quad (37)$$

- (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.

$$V_{\text{eff}}(r) = V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} \quad (38)$$

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

$$KE = \underbrace{\frac{1}{2} m v_r^2}_{\text{radial KE}} + \underbrace{\frac{L^2}{2mr^2}}_{\text{angular KE}} \quad (39)$$

where $L = m v_\perp r$ is the angular momentum. For a wave function with agular quantum number ℓ the angular momentum $\mathbb{L}^2 = \ell(\ell+1)\hbar^2$ as discussed in Eq. (28). 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

$$F_C = m \frac{v^2}{r} \hat{r} = \frac{L^2}{mr^3} \hat{r} \quad (40)$$

where $L = mvr$ is the angular momentum. For a state with angular quantum number the angular momentum $\overline{L}^2 = \ell(\ell + 1)\hbar^2$ as discussed near Eq. (28). Then we note that the “force” due to this extra potential

$$F_C = -\frac{\partial}{\partial r} \frac{\ell(\ell + 1)\hbar^2}{2mr^2} \hat{r} = \frac{\overline{L}^2}{mr^3} \hat{r} \quad (41)$$

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

$$\overline{PE} = \int_0^\infty \frac{-e^2}{4\pi\epsilon_0 r} P(r) dr \quad (42)$$

and

$$\bar{r} = \int_0^\infty r P(r) dr \quad (43)$$

The variance in the radius is

$$(\Delta r)^2 \equiv \overline{r^2} - \bar{r}^2 \quad (44)$$

5. The average kinetic energy is

$$\overline{KE} = \int_0^\infty u_{nl}^* \left[\underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2}}_{\text{radial KE}} + \underbrace{\frac{\ell(\ell + 1)\hbar^2}{2mr^2}}_{\text{angular KE}} \right] u_{nl} dr \quad (45)$$

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 (not really part of exam):

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

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi) \quad (46)$$

so that

$$\mathbb{L}^2 Y_{lm} = \ell(\ell + 1)\hbar^2 Y_{lm} \quad (47)$$

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

$$\mathbb{L}_z Y_{lm} = m\hbar Y_{lm} \quad (48)$$

where the angular momentum squared operator and are

$$\mathbb{L}^2 = -\hbar^2 \left(\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (49)$$

$$\mathbb{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (50)$$

ℓ	m	$\Phi_m(\phi)$	$\Theta_{lm}(\theta)$	
0	0	1	1	
1	0	1	$\sqrt{3} \cos(\theta)$	
1	± 1	$e^{\pm i\phi}$	$\sqrt{\frac{3}{2}} \sin(\theta)$	(51)
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	$e^{\pm i2\phi}$	$\frac{1}{2} \sqrt{\frac{15}{2}} \sin^2(\theta)$	

Hydrogen Atom

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

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (52)$$

- The energies are

$$E_{n\ell} = -\frac{\hbar^2}{2ma_0^2} \frac{Z^2}{n^2} = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^2}{n^2} \quad (53)$$

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	$\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$
2	0	0	2s	1	$\frac{1}{\sqrt{32\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{\sqrt{32\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	2p	$\sqrt{3} \cos(\theta)$	$\frac{1}{\sqrt{96\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{\sqrt{32\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos(\theta)$
2	1	± 1	2p	$e^{\pm i\phi} \sqrt{\frac{3}{2}} \sin(\theta)$	$\frac{1}{\sqrt{96\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{\sqrt{64\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin(\theta) e^{\pm i\phi}$

(54)

- An integral which comes up a lot is

$$\int_0^\infty dx x^n e^{-x} = n! \quad (55)$$

- For $n = 3$ we will quote the R_{nl} only. For the necessary table of Θ_{lm} and Φ_m see Eq. 51. Here

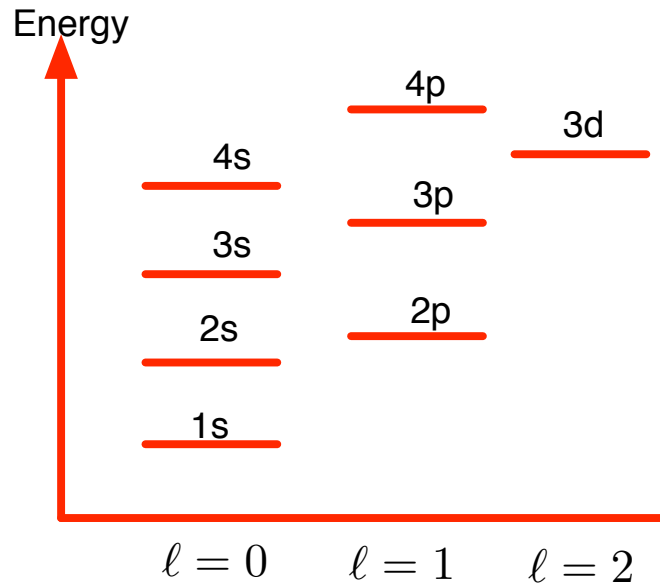
$$\rho \equiv \frac{2r}{3a_0} \quad (56)$$

n	ℓ	R_{nl}
3	0	$\sqrt{\frac{40}{(4\pi)6!}} \left(\frac{2}{3a_0}\right)^{3/2} \frac{1}{2} (6 - 6\rho + \rho^2) e^{-\rho/2}$
3	1	$\sqrt{\frac{5}{(4\pi)6!}} \left(\frac{2}{3a_0}\right)^{3/2} (4 - \rho) \rho e^{-\rho/2}$
3	2	$\sqrt{\frac{1}{(4\pi)6!}} \left(\frac{2}{3a_0}\right)^{3/2} \rho^2 e^{-\rho/2}$

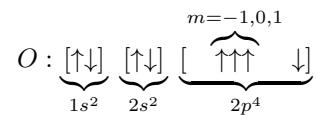
(57)

Atoms

- Electrons fill up orbitals one by one. There are some things to know when filling up the shells
 - After filling the $3p$ orbital, one starts filling the $4s$ orbital before filling the $3d$ orbital. This is because the $4s$ state is actually lower than the $3d$ state as shown below. They are very close however.



- **Hunds Rule.** Take filling up the $3p$ orbital for example. When filling up the $2p$ orbital one first fills up the m levels with the same spin, and then one starts the process again for the next spin. See Fig. 9.15 of the book for a good explanation. Thus the structure of Oxygen (with $Z = 8$) is the following



where each arrow represents an electron.