Fundamentals in Biophotonics

Photon /wave particle duality

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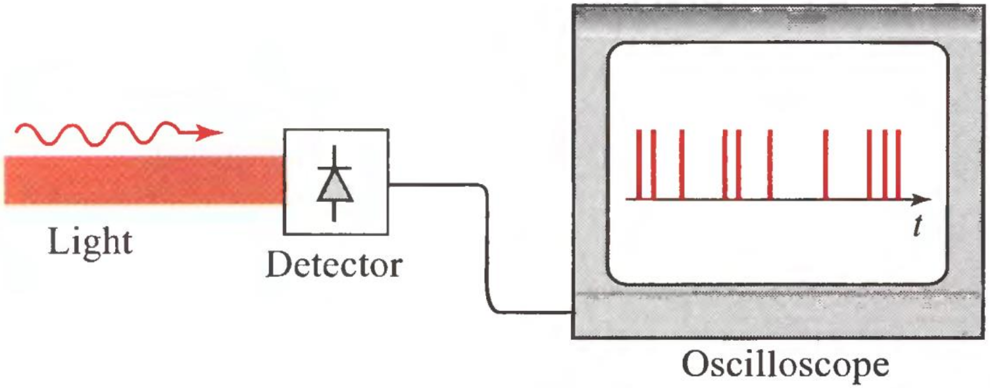
Photon Streams

- The temporal pattern of such photon registrations can be highlighted by examining
- the temporal and spatial behavior separately. Consider the use of a detector with good temporal resolution that integrates light over a finite area A



$$P(t) = \int_A I(\mathbf{r}, t)\, dA.$$

Photon registrations at random localized instants of time for a detector that integrates light over an area A.

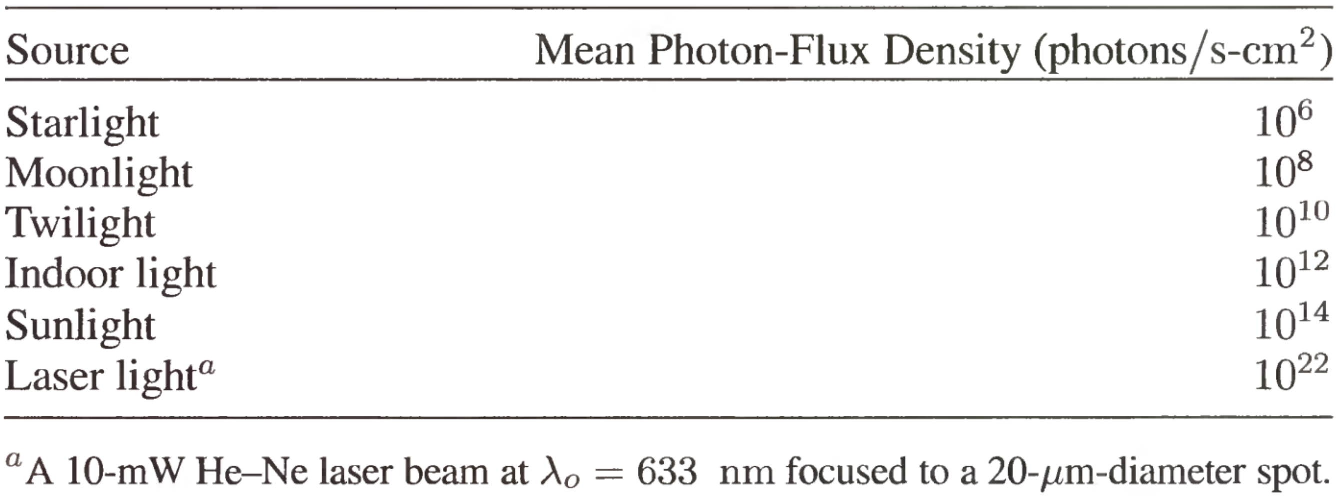
Mean Photon-Flux Density

Monochromatic light of frequency v and classical intensity I(r) (Watts/cm ^{2}) carries a mean photon-flux density

$$\phi(\mathbf{r}) = \frac{I(\mathbf{r})}{h\nu}.$$

Mean Photon Flux Density/ Mean Photon Flux

- Typical values of q; r for some common sources of light



Source	Mean Photon-Flux Density (photons/s-cm^2)
Starlight	10^6
Moonlight	10^8
Twilight	10^{10}
Indoor light	10^{12}
Sunlight	10^{14}
Laser light[a]	10^{22}

[a] A 10-mW He–Ne laser beam at $\lambda_o = 633$ nm focused to a 20-μm-diameter spot.

The mean photon flux Φ (units of photons /s) is obtained by integrating the mean photon-flux density over a specified area

$$\Phi = \int_A \phi(\mathbf{r})\, dA = \frac{P}{h\overline{\nu}},$$

As an example, 1 nW of optical power, at a wavelength λ 200 nm, delivers to an object an average photon flux $\Phi = 10^9$ photons per second.

Mean Number of photons

- The mean number of photons **n** detected in the area A and in the time interval T is obtained by multiplying the mean photon flux Φ in by the time duration

$$\overline{n} = \Phi T = \frac{E}{h\overline{\nu}},$$

Classical		Quantum	
Optical intensity	$I(\mathbf{r})$	Photon-flux density	$\phi(\mathbf{r}) = I(\mathbf{r})/h\overline{\nu}$
Optical power	P	Photon flux	$\Phi = P/h\overline{\nu}$
Optical energy	E	Photon number	$\overline{n} = E/h\overline{\nu}$

Time Varying Light

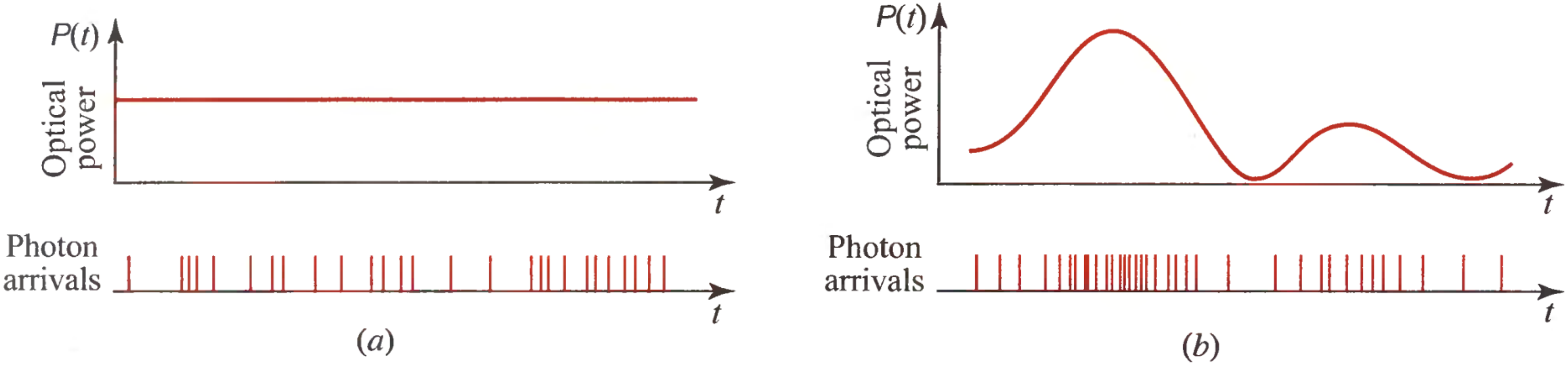
$$\phi(\mathbf{r}, t) = \frac{I(\mathbf{r}, t)}{h\overline{\nu}}.$$

$$\Phi(t) = \int_A \phi(\mathbf{r}, t)\, dA = \frac{P(t)}{h\overline{\nu}}, \overline{n} = \int_0^T \Phi(t)\, dt = \frac{E}{h\overline{\nu}},$$

Randomness of Photon Flow

- For photon streams, the classical intensity **I(r,t)** determines the mean photon- flux density **ϕ(r,t).** The properties of the light source determine the fluctuations

- the times at which the photons are detected are random, their statistical behavior determined by the source,



(a) Constant optical power and the corresponding **random photon arrival times**.

(b) Time-varying optical power and the corresponding random photon arrival times

Randomness of Photon Flow

- An understanding of photon-number statistics is important for applications such as reducing noise in weak images and optimizing optical information transmission.

- **Coherent light** has a constant optical power P. The corresponding mean photon flux Φ=P/hν (photons/s) is also constant, but the actual times of registration of the photons are random. An expression for the **probability distribution p(n)** can be derived under the assumption that the registrations of photons are statistically independent. The result is the **Poisson distribution**

$$p(n) = \frac{\overline{n}^{\,n} \exp(-\overline{n})}{n!}, \qquad n = 0, 1, 2, \ldots$$

- It is not difficult to show   that the mean of the Poisson distribution is indeed n and its variance is equal to its mean:

$$\sigma_n^2 = \overline{n}.$$

Signal to Noise Ratio

- **The randomness of the number of photons** constitutes a fundamental source of noise that we have to account for when using light to transmit a signal. Representing the mean of the signal as **n,** and its noise by **the root mean square value is** σn, a useful measure of the performance of light as an information-carrying medium is the signal-to-noise ratio (SNR). The SNR of the random number n is defined as

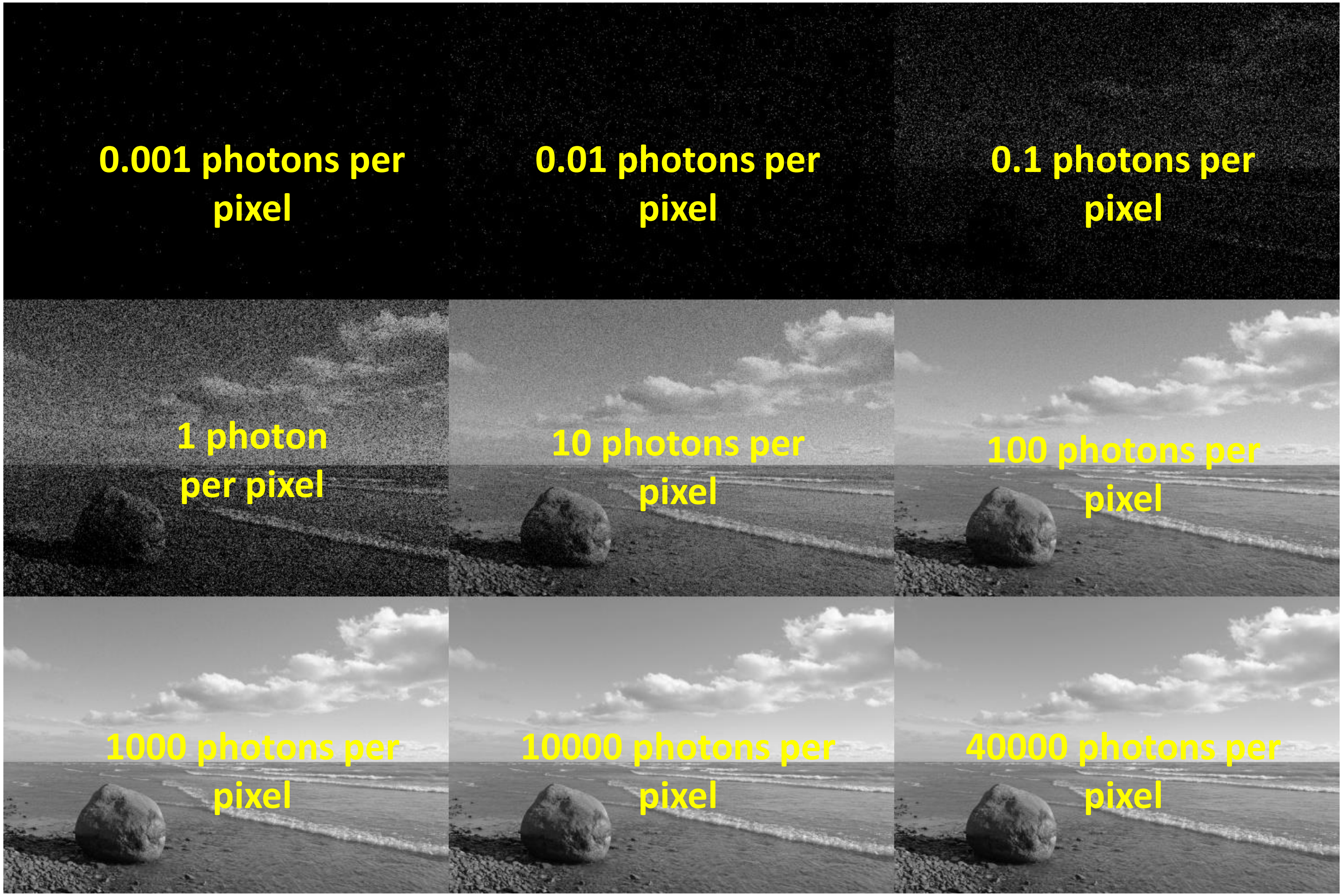
$$\mathrm{SNR} = \frac{(\mathrm{mean})^2}{\mathrm{variance}} = \frac{\bar{n}^2}{\sigma_n^2}.$$

For the Poisson distribution

$$\mathrm{SNR} = \bar{n},$$

so that the signal-to-noise ratio **increases linearly with the mean number of photon counts.**

Photon Shot Noise/ Exposure dependent

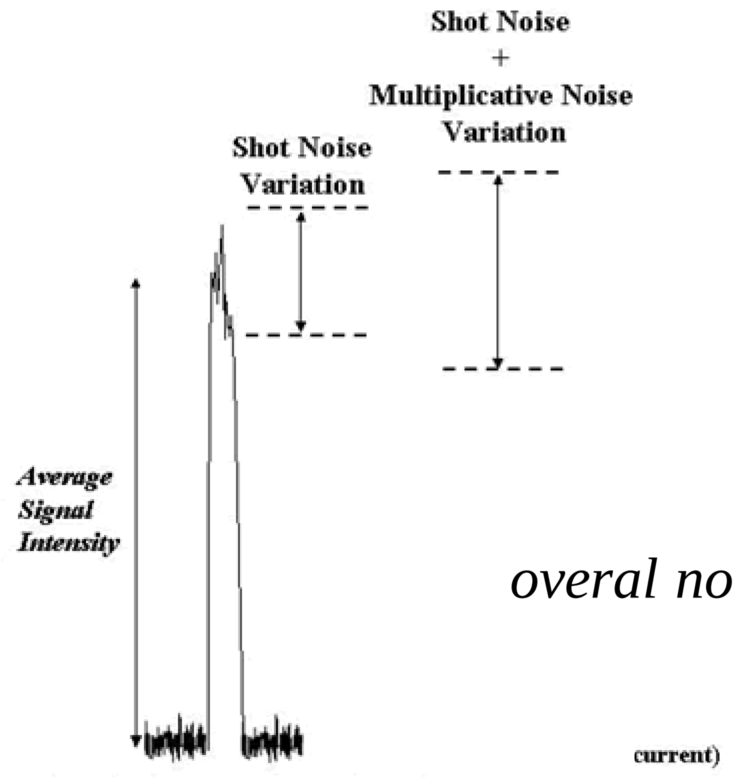


A photon noise simulation, using a sample image as a source and a per-pixel Poisson process to model an otherwise perfect camera (quantum efficiency = 1, no read-noise, no thermal noise, etc).

Noise Sources of a Detector

Photon Shot Noise – Counting statistics of the signal photons

- -Originates from the Poisson distribution of signal photons as a function of time
- -Random arrival of photons and electron is governed by Poisson distribution



- Dark Current Noise – Counting statistics of spontaneous electron generated in the device
- Johnson Noise – Thermally induced current in the transimpedence amplifier

$$overal\ noise = \sqrt{(readnoise)^2 + (darknoise)^2 + (shotnoise)^2}$$

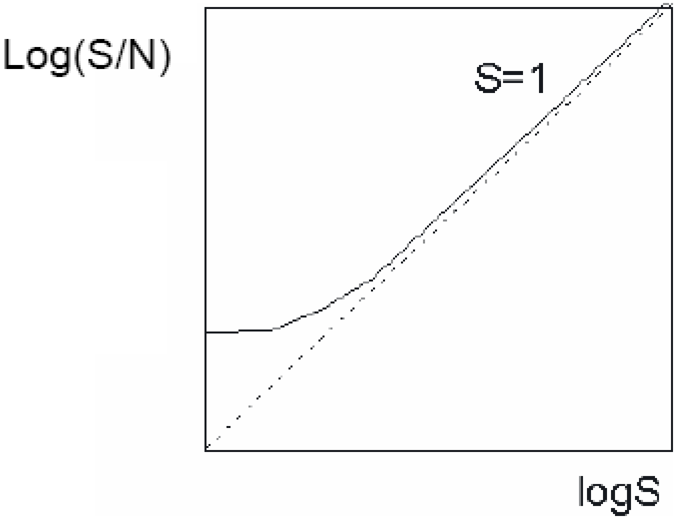
Photon Shot Noise

- Shot noise is white noise, just like Johnson noise. Does not exist unless current is driven through the device.
- This is termed **“white noise”** why?
- Because, like in white light**, all frequencies are equally represented**

- Standard deviation (or noise) and the photon noise limited Signal-to-Noise-Ratio (SNR) associated with detecting a mean of ‘N’ photons are given by

$$Noise\,(photon) \approx \sqrt{N}$$

$$SNR(photon) = \frac{Signal}{Noise} \approx \frac{N}{\sqrt{N}} = \sqrt{N}$$



- Means to **enhance** S/N
  - – Signal averaging: internally or externally
  - – Signal smoothing: boxcar averaging, moving average, polynomial smoothing (**keyword: convolution**)
  - – Filtering in the frequency domain:

Why does the light interacts with the matter?

- Light interacts with matter because matter contains electric charges. The time-varying electric field ***of light exerts forces on the electric charges and dipoles in atoms, molecules, and solids, causing them to vibrate so that they undergo acceleration.***

- **Vibrating electric charges absorb and emit light.**

- Atoms, molecules, and solids have ***specific allowed energy levels and bands that are determined by the rules of quantum mechanics.***

- A photon may interact with an atom if its **energy *matches* the difference between two atomic energy levels**.

- ***Absorption***
- ***Emission***
- ***Stimulated emission***

Energy Levels

- The behavior of a single nonrelativistic particle of mass m (an electron, for example), subject to a potential **V(r, t),** is governed by a complex **wavefunction Ψ(r, t)** that satisfies the Schrodinger equation

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t)+V(\mathbf{r},t)\Psi(\mathbf{r},t)=-j\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}.}$$

Special case of the potential energy of the electron-proton system is electrostatic and in the absence of the time varying potential

The energy levels of a hydrogen-like atom comprising a nucleus of charge +Ze and a single electron of charge -e and mass m, where Z is the atomic number, are determined by inserting the Coulomb potential

$$\boxed{V(r)=-\frac{Ze^2}{4\pi\varepsilon_0 r}}$$

Time independent Schrödinger Equation

$$\Psi(\mathbf{r},t)=\psi(\mathbf{r})\exp[j(E/\hbar)t],$$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r}).}$$

Schrodinger equation

> “Where did we get that (equation) from? Nowhere. It is not possible to derive it from anything you know. It came out of the mind of Schrödinger.”

Richard Feynman

Erwin Schrödinger

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})\exp[j(E/\hbar)t],$$

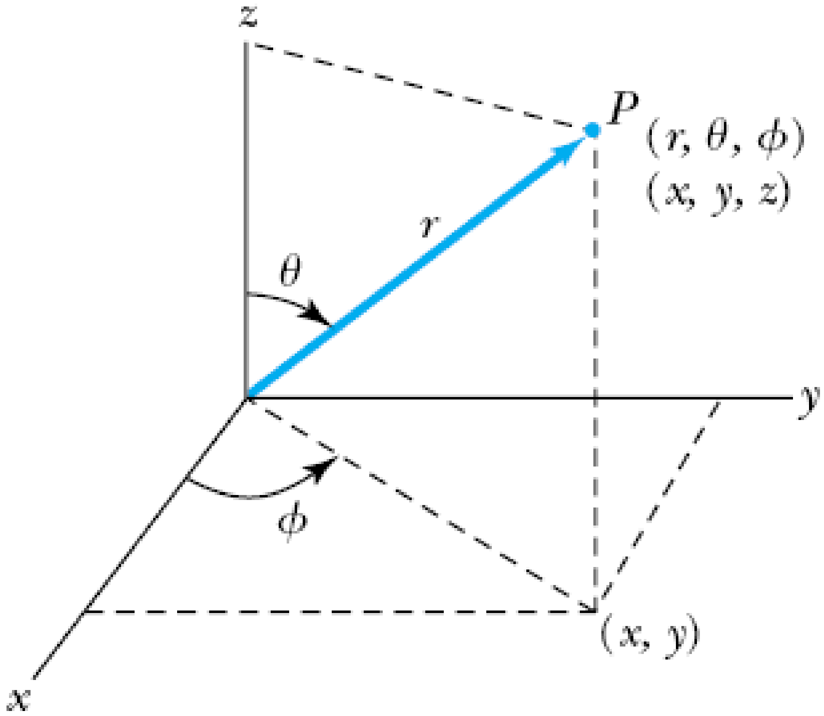
position-space wave function

Energy Levels

- Use the three-dimensional time-independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right]=E-V(r)$$

The potential (central force) $V(r)$ depends on the distance r between the proton and electron. ***Transform to spherical polar coordinates because of the radial symmetry***



$$x = r\sin\theta\cos\varphi$$

$$y = r\sin\theta\sin\varphi$$

$$z = r\cos\theta$$

$$r = \sqrt{x^2+y^2+z^2}$$

$$\theta = \cos^{-1}\frac{z}{r} \quad \text{(Polar angle)}$$

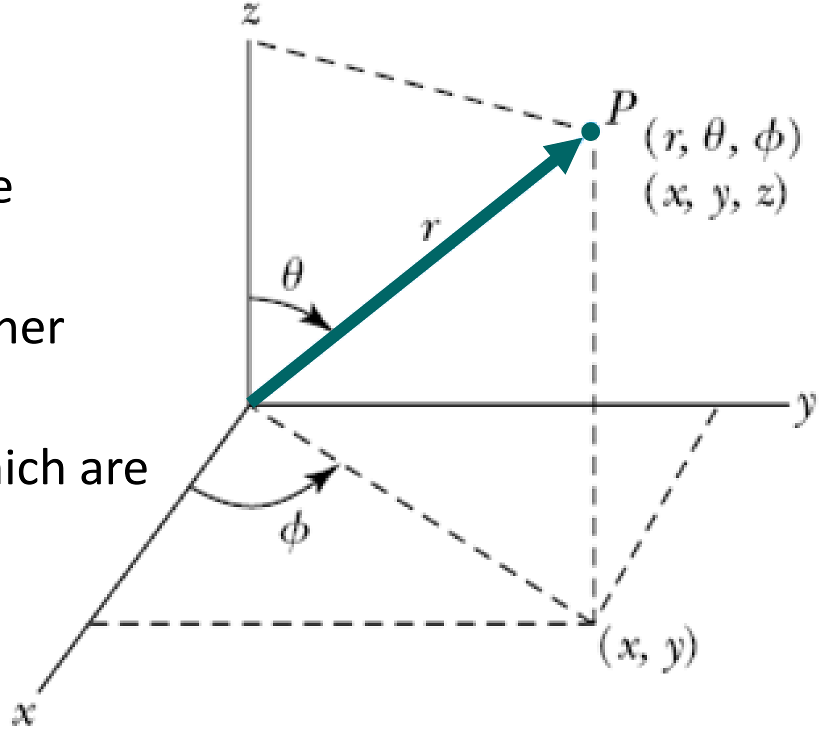
$$\varphi = \tan^{-1}\frac{y}{x} \quad \text{(Azimuthal angle)}$$

The Schrödinger Equation in Spherical Coordinates

- Transformed into spherical coordinates, the Schrödinger equation becomes

$$\boxed{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+\frac{2\mu}{\hbar^2}(E-V)\psi=0}$$

Atomic energy levels are established by the potential energies of the electrons in the presence of the atomic nucleus and the other electrons, as well as by forces involving the **orbital** and **spin angular momenta**, which are usually much weaker than the inter-actions involving charges.



Hydrogen atom-energy levels

- The wave function ψ is a function of r, θ, ϕ. This is a potentially complicated function.

- Assume optimistically that ψ is **separable**, that is, a product of three functions, each of one variable only

$$\psi(r,\theta,\phi)=R(r)f(\theta)g(\phi)$$

$$\frac{\partial\psi}{\partial r}=fg\frac{\partial R}{\partial r}\qquad\frac{\partial\psi}{\partial\theta}=Rg\frac{\partial f}{\partial\theta}\qquad\frac{\partial^2\psi}{\partial\phi^2}=Rf\frac{\partial^2 g}{\partial\phi^2}$$

This would make life much simpler—and it turns out to work!

Start with Schrodinger's Equation:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}+\frac{2\mu}{\hbar^2}(E-V)\psi=0$$

Substitute:

$$\frac{\partial\psi}{\partial r}=fg\frac{\partial R}{\partial r}\qquad\frac{\partial\psi}{\partial\theta}=Rg\frac{\partial f}{\partial\theta}\qquad\frac{\partial^2\psi}{\partial\phi^2}=Rf\frac{\partial^2 g}{\partial\phi^2}$$

Hydrogen atom-energy levels -Solution of the Schrödinger Equation

$$\frac{fg}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{Rg}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\frac{Rf}{r^2\sin^2\theta}\frac{\partial^2 g}{\partial\phi^2}+\frac{2\mu}{\hbar^2}(E-V)Rfg=0$$

Multiply both sides by $-r^2\sin^2\theta/Rfg$:

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2\mu}{\hbar^2}r^2\sin^2\theta(E-V)-\frac{\sin\theta}{f}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)=\frac{1}{g}\frac{\partial^2 g}{\partial\phi^2}$$

- r and θ appear only on the left side and ϕ appears only on the right side.
- The left side of the equation cannot change as ϕ changes.
- The right side cannot change with either r or θ.

- Each side needs to be equal to a **constant** for the equation to be true.
- Set the constant to be $-m_\ell^2$

$$\frac{d^2 g}{d\phi^2}=-m_\ell^2 g$$ **azimuthal equation**

-

Hydrogen atom-energy levels - Solution of the Schrödinger Equation

- Sines and cosines satisfy this equation, but it is convenient to choose the solution to be

$$g = e^{im_\ell \phi} \qquad \frac{d^2 g}{d\phi^2} = -m_\ell^{\ 2} g$$

$$g = e^{im_\ell \phi}$$

satisfies the azimuthal equation for any value of ***m*$_\ell$**.
The solution must be single valued to be a valid solution for any ϕ:

$$g(\phi) = g(\phi + 2\pi)$$

Specifically: $$g(\phi = 0) = g(\phi = 2\pi)$$

So: $$e^0 = e^{2\pi i m_\ell}$$

m_ℓ must be an integer (positive or negative) for this to be true.

Hydrogen atom-energy levels - Solution of the Schrödinger Equation

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2\mu}{\hbar^2}r^2\sin^2\theta(E-V)-\frac{\sin\theta}{f}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)=\frac{1}{g}\frac{\partial^2 g}{\partial\phi^2}$$

- Now set the left side equal to $-m_\ell{}^2$:

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-\frac{2\mu}{\hbar^2}r^2\sin^2\theta(E-V)-\frac{\sin\theta}{f}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)=-m_\ell{}^2$$

Rearrange it and divide by $\sin^2(\theta)$:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)=\frac{m_\ell{}^2}{\sin^2\theta}-\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)$$

Now, the left side depends only on r, and the right side depends only on θ. We can use the same trick again!

Hydrogen atom-energy levels - Solution of the Schrödinger Equation

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)=\frac{m_\ell^2}{\sin^2\theta}-\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)$$

- Set each side equal to the constant $\ell(\ell+1)$.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu}{\hbar^2}\left[E-V-\frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]R=0$$

Radial equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\left[\ell(\ell+1)-\frac{m_\ell^2}{\sin^2\theta}\right]f=0$$

Angular equation

We've separated the Schrödinger equation **into three ordinary second-order differential equations, each containing only one variable.**

Solution of the Radial Equation for H atom

- The radial equation is called the **associated Laguerre equation** and the solutions R are called **associated Laguerre functions**. There are infinitely many of them, for values of $n = 1, 2, 3, \ldots$

- Assume that the ground state has $n = 1$ and $\ell = 0$. Let's find this solution.
- The radial equation becomes:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu}{\hbar^2}(E-V)R=0$$

- The derivative of $r^2\frac{dR}{dr}$ yields two terms: $\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R=0$

- Try a solution
- A is a normalization constant.
- a_0 is a constant with the dimension of length.
- Take derivatives of R and insert them into the radial equation.

$$R(r)=Ae^{-r/a_0}$$

Solution of the Radial Equation for H

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R=0 \Rightarrow \left(\frac{1}{a_0{}^2}+\frac{2\mu}{\hbar^2}E\right)+\left(\frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2}-\frac{2}{a_0}\right)\frac{1}{r}=0$$

- To satisfy this equation for any r, both expressions in parentheses must be zero.

Set the second expression equal to zero and solve for a_0:

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

Set the first expression equal to zero and solve for E:

$$E=-\frac{\hbar^2}{2\mu a_0{}^2}=-E_0$$

Both are equal to the Bohr results!

There are many solutions to the radial wave equation, one for each positive integer, n.

The result for the quantized energy is:

$$\boxed{E_n=\frac{-\mu}{2}*Z^2\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)\frac{1}{n^2}=-\frac{E_0}{n^2}}$$

Quantum numbers

- The four quantum numbers-are discrete sets of integers or half-integers.

  –n: Principal quantum ***number-The first describes the electron shell, or energy level, of an atom***

  –ℓ : Orbital angular momentum quantum number-as **the angular quantum number or orbital quantum number) describes the subshell, and gives the magnitude of the orbital angular momentum through the relation**

$$L^2 = \hbar(l+1)$$

  –m_ℓ:Magnetic (azimuthal) quantum number

  (refers, to the direction of the angular momentum vector. The magnetic quantum number m does not affect the electron's energy, but it does affect the probability cloud)- magnetic quantum number determines the energy shift of an atomic orbital due to an external magnetic field-Zeeman effect

  -s spin- intrinsic angular momentum Spin "up" and "down" allows two electrons for each set of spatial quantum numbers.

The restrictions for the quantum numbers:

- $n = 1, 2, 3, 4, \ldots$
- $\ell = 0, 1, 2, 3, \ldots, n - 1$
- $m_\ell = -\ell, -\ell + 1, \ldots, 0, 1, \ldots, \ell - 1, \ell$
-

–Equivalently:

$n > 0$

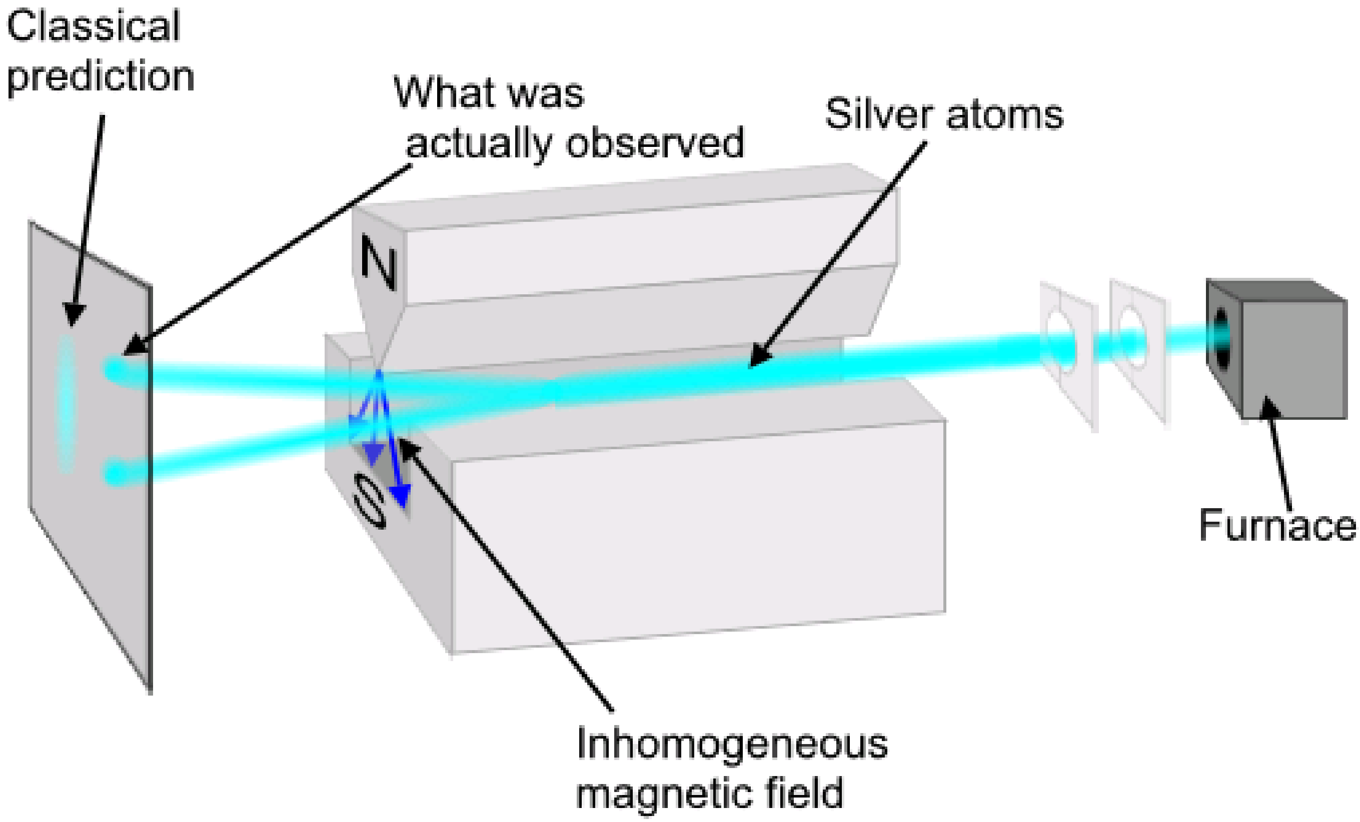
$\ell < n$

$|m_\ell| \leq \ell$

The energy levels are:

$$E_n = -\frac{E_0}{n^2}$$

Stern-Gerlach experiment



If the particles were classical spinning objects, one would expect the distribution of their spin angular momentum vectors to be random and continuous. Each particle would be deflected by a different amount, producing some density distribution on the detector screen. Instead, the particles passing through the Stern–Gerlach apparatus are deflected either up or down by a specific amount. This was a measurement of the quantum observable now known as spin, which demonstrated possible outcomes of a measurement where the observable has point spectrum.

Hydrogen Atom Radial Wave Functions

- First few radial wave functions $R_{n\ell}$

Sub-scripts on R specify the values of n and ℓ.

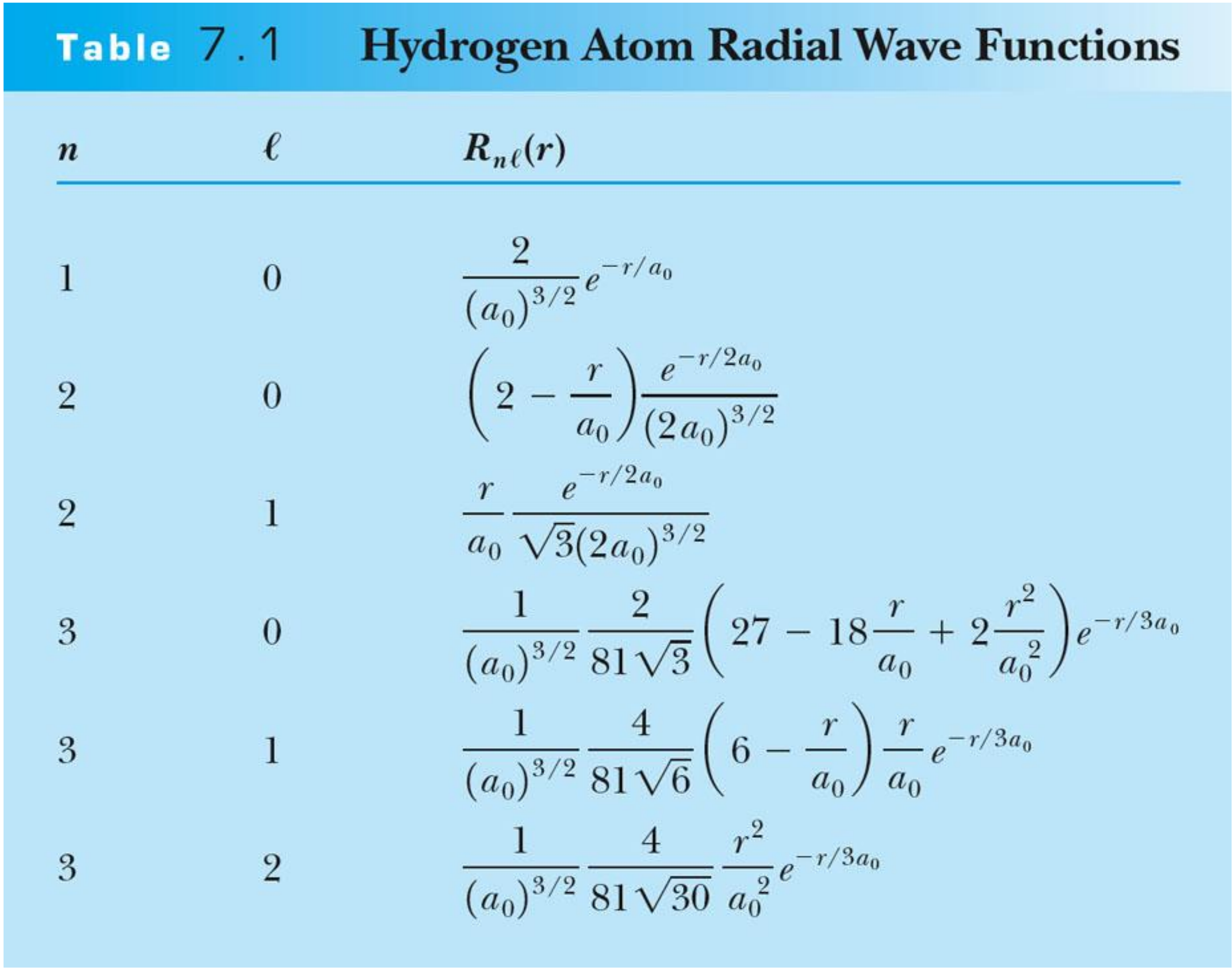


Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{6}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$

Solution of the Angular and Azimuthal Equations

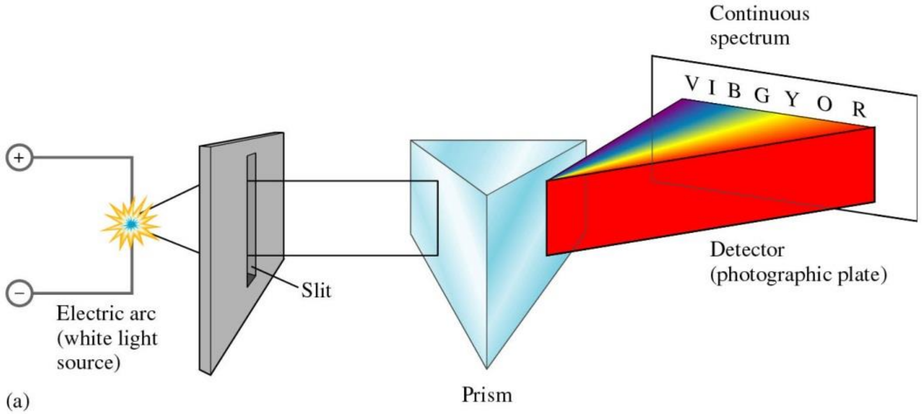
- The radial wave function R and the spherical harmonics Y determine the probability density for the various quantum states. The total wave function $\psi(r, \theta, \phi)$
- depends on n, ℓ, and m_ℓ.
- The wave function becomes

$$\boxed{\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r)\, Y_{n\ell m_\ell}(\theta, \phi)}$$

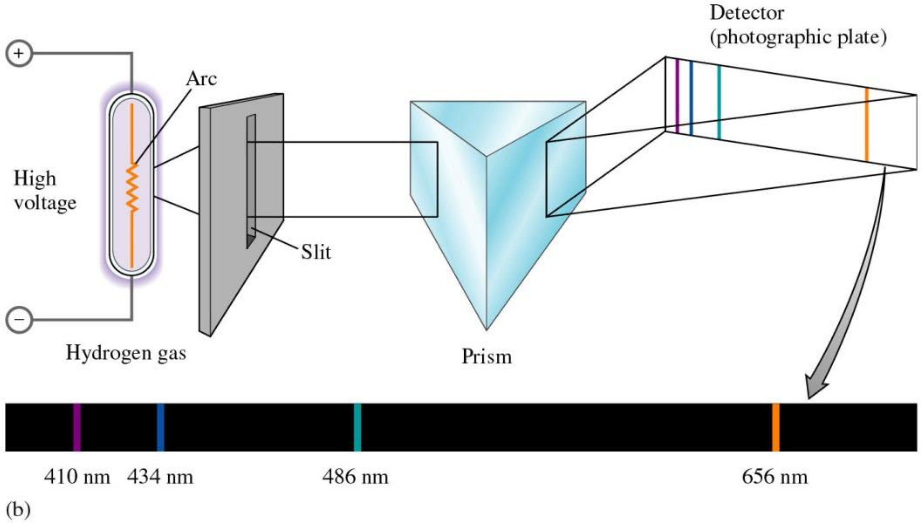
The four quantum numbers *n*, *ℓ*, *m*, and *s* specify the complete and unique quantum state of a single electron in an atom called its wavefunction or orbital.

Bohr atom model

- In 1913, the Danish scientist Niels Bohr proposed an improvement. In his model, he placed each electron in a **specific** energy level.



Light Bulb

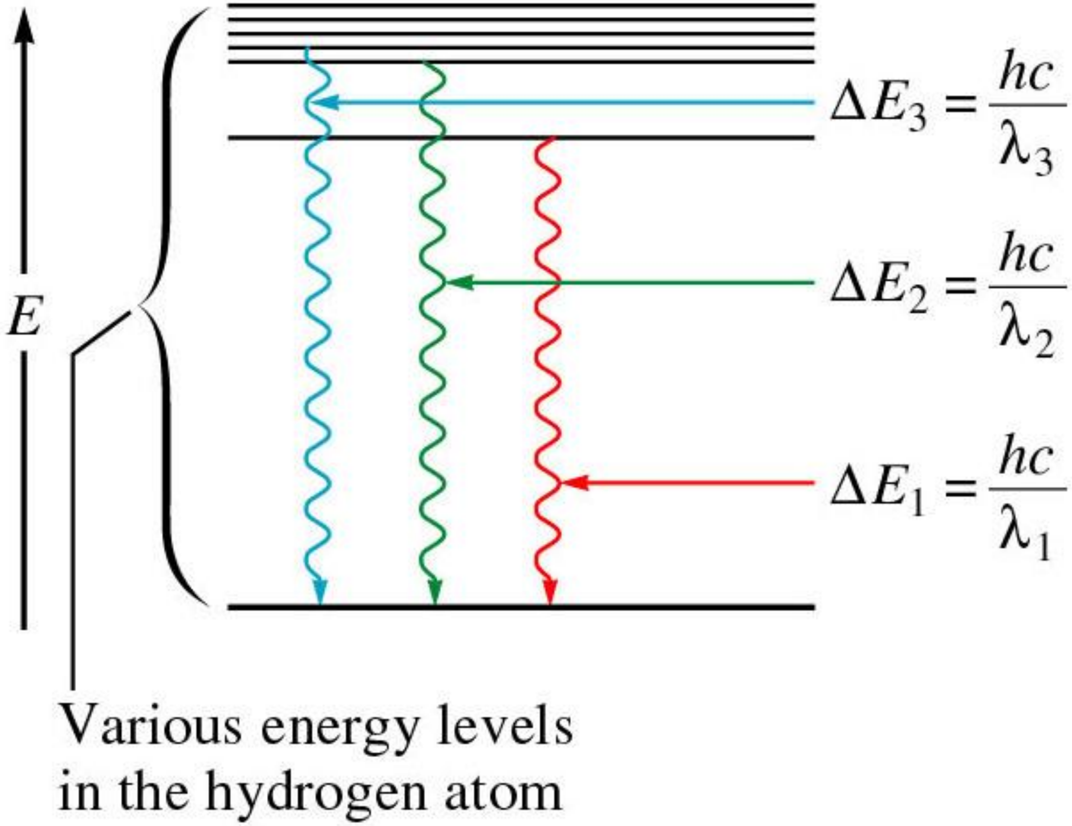


Hydrogen Lamp

Quantized, not continuous

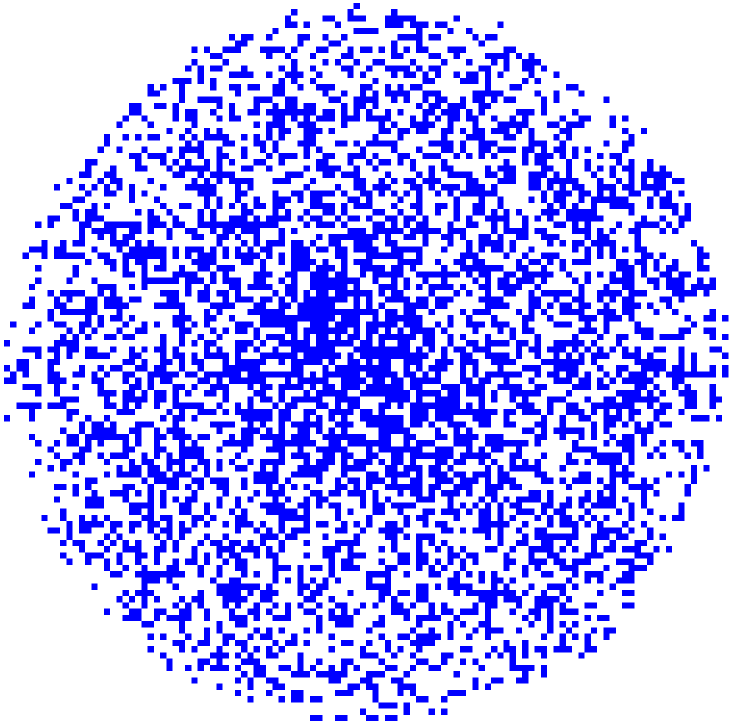
Emission spectrum of Hydrogen atom

- We can use the emission spectrum to determine the energy levels for the hydrogen atom.



Bohr atom model

- According to Bohr's atomic model, electrons move in definite orbits around the nucleus, much like planets circle the sun. These orbits, or energy levels, are located at certain distances from the nucleus
- In fact, it is impossible to determine the exact location of an electron. The probable location of an electron is based on how much energy the electron has.
- According to the modern atomic model, at atom has a small positively charged nucleus surrounded by a large region in which there are enough electrons to make an atom neutral.



Probability Distribution Functions

- We use the wave functions to calculate the probability distributions of the electrons.
- The "position" of the electron is spread over space and is not well defined.
- We may use the radial wave function $R(r)$ to calculate radial probability distributions of the electron.
- The probability of finding the electron in a differential volume element $d\tau$ is:

$$dP = \psi^*(r,\theta,\phi)\ \ \psi(r,\theta,\phi)\ \ dx\, dy\, dz$$

where the differential volume element in spherical polar coordinates is

$$dx\, dy\, dz = r^2 \sin\theta\ dr\ d\theta\ d\phi$$

At the moment, we'll consider only the radial dependence. So we should integrate over all values of θ and ϕ:

$$P(r)\ dr = r^2 R^*(r) R(r)\ dr \int_0^{\pi} \left| f(\theta) \right|^2 \sin\theta\, d\theta \int_0^{2\pi} \left| g(\phi) \right|^2 d\phi$$

The θ and ϕ integrals are just constants.

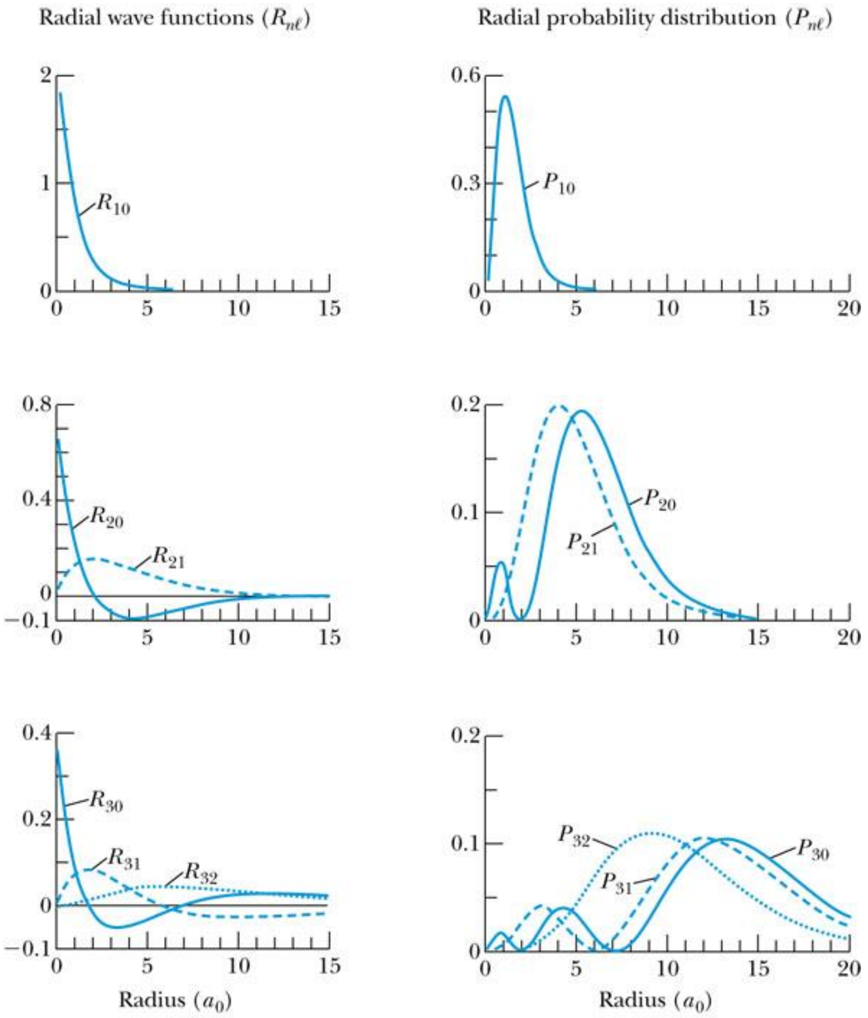
Probability Distribution Functions

- So the radial probability density is $P(r) = r^2\,|R(r)|^2$ and it depends only on n and ℓ.

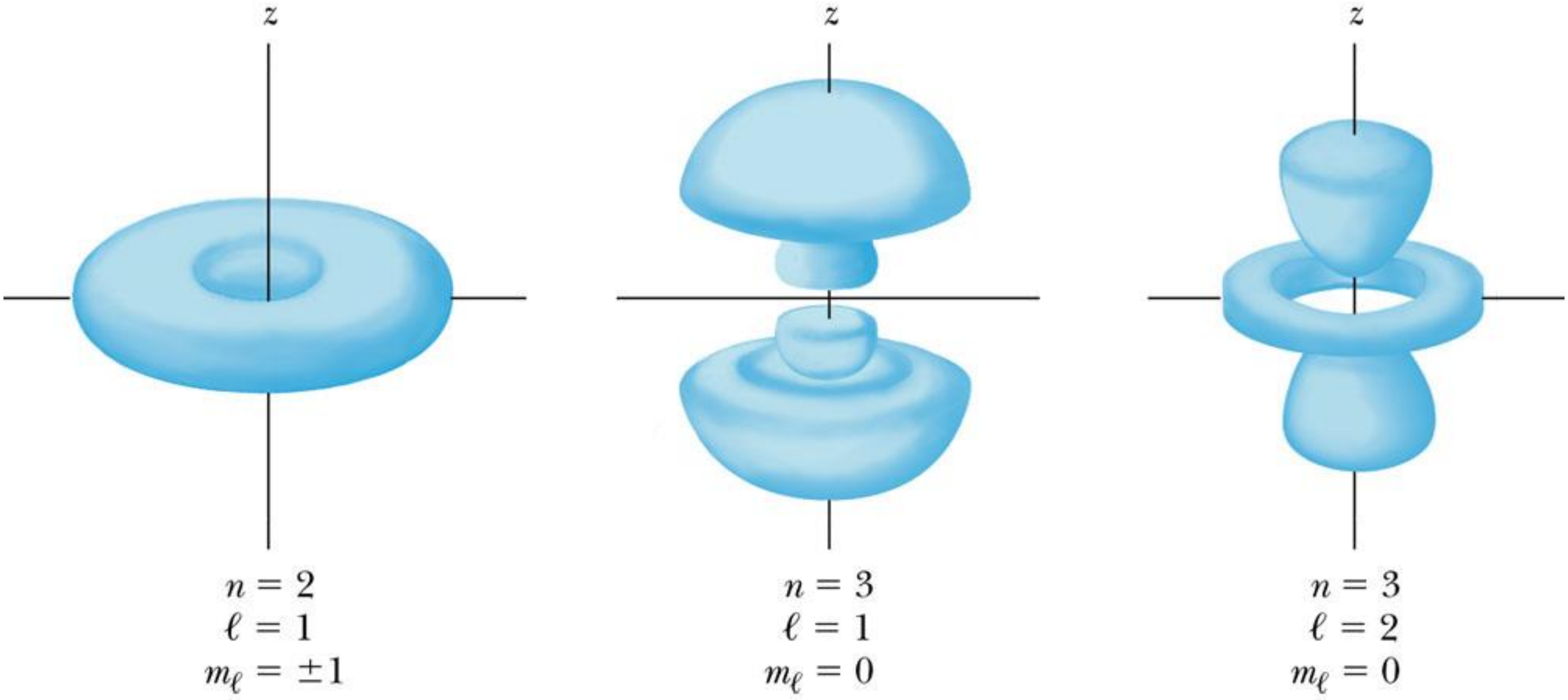
$$P(r)\,dr = r^2 \left|R(r)\right|^2\,dr$$

$R(r)$ and $P(r)$ for the lowest-lying states of the hydrogen atom.

Note that R_{n0} is maximal at $r = 0$! But the r^2 factor reduces the probability there to 0. Nevertheless, there's a nonzero probability that the electron is inside the nucleus.



Probability Distribution Functions



In chemistry and spectroscopy, "ℓ = 0" is called an s orbital, "ℓ = 1" a p orbital, "ℓ = 2" a d orbital, and "ℓ = 3" an f orbital. The value of ℓ ranges from 0 to *n* − 1, because the first p orbital (ℓ = 1) appears in the second electron shell (*n* = 2), the first d orbital (ℓ = 2) appears in the third shell (*n* = 3), and so on:[4]