量子力学
Quantum mechanics

School of Physics and Information Technology
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Chapter 4

QUANTUM MECHANICS IN THREE DIMENSIONS

4.1 Schrödinger Equation in Spherical Cordinations

(1) The generalization of the Schrödinger Equation from one-dimensional to three-dimensional is straightward. The SE says

the Hamiltonian operator H is obtained from the classical energy

by the standard prescription (applied now to y,z as well as x)

As

or, for short

where

Thus

where

is the Laplacian, in

Cartesian coordinates.

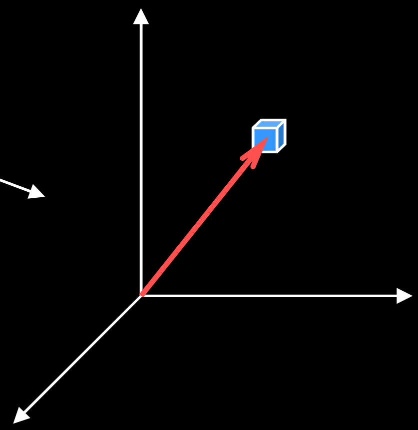
And in 3-dimensional space

as well as

(2) The probability of finding the particle in the infinitesimal volume d^3r,

is

(3) Therefore the normalization condition reads



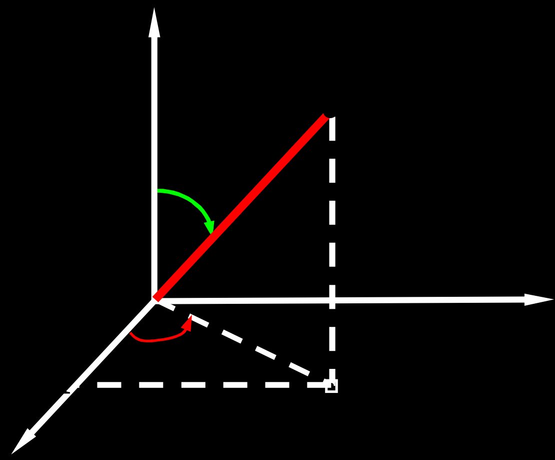
(4) If the potential is time-independent, the time-independent Schrodinger equation reads

and there will be a complete set of stationary states

The general solution to the (time-dependent) Schrodinger equation is

4.1.1 Separation of Variables

(1) Spherical coordinates



Cartesian coordinates:

Spherical coordinates:

In spherical coordinates the Laplacian takes the form

The time-independent Schrodinger equation in Cartesian coordinates

In spherical coordinates

We begin by looking for solutions that are separable into products:

Putting this into above equation, we have

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r}\frac{d}{dr}\left(\right.\right.$$

Dividing by RY and multiplying by

The term on the left hand depends only on r, whereas the right depends only on θ φ; accordingly, each must be a constant, which is in the form l(l+1):

Spherically symmetric potential

4.1.2 The Angular Equation

Solution of Y : Equation 4.17 determines *Y* function as

Multiplying above equation by $Y\sin^2\theta$, it becomes:

As always, we try separation of variables:

Plugging this in, and dividing by Y, we find

The first term is a function only of θ, and the second is a function only of , so each must be a constant. This time I will call the separation constant m^2:

(1) The equation is easy to solve:

Now, when advances by 2π, we return to the same point in space, so it is natural to require that

In other words,

From this it follows that m must be an integer:

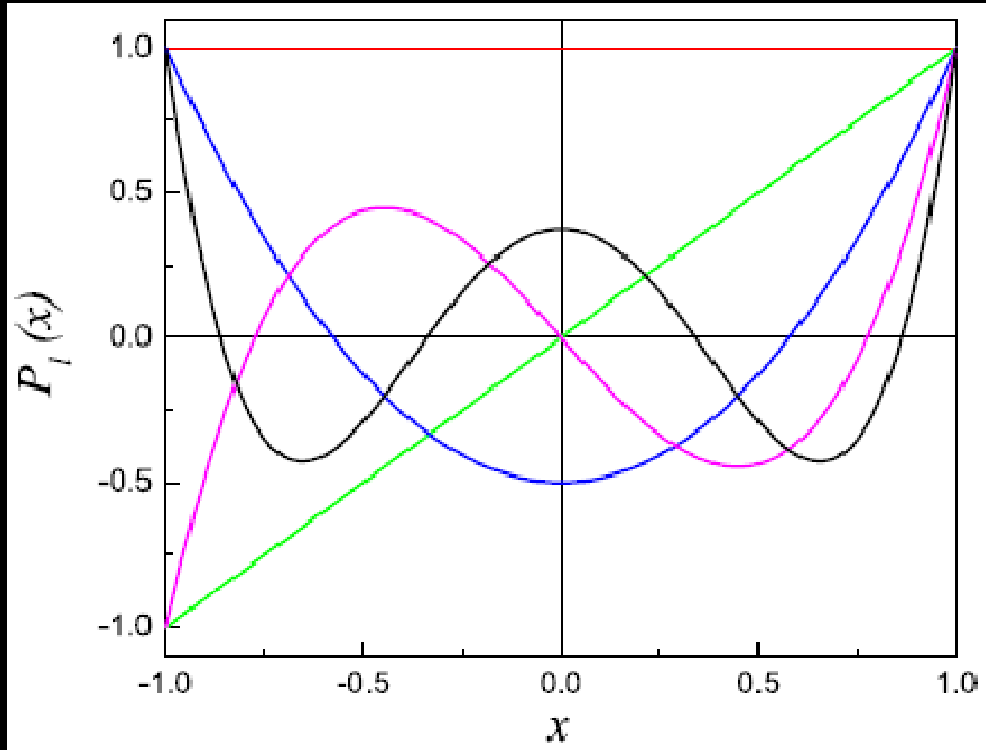
(2) The equation is not simple.

Turn into x by:

Above equation is *l*th-order associated Legendre equation.

Therefore, the solution of Θ is

where $P^m{}_l$ is the associated Legendre function, defined by and $P_l(x)$ is the lth Legendre polynomial, defined by the Rodrigues formula:



$P_4(x)$

❖ $P_l(x)$ is a polynomial (of degree l) in x, and is even or odd according to the *parity* of l.

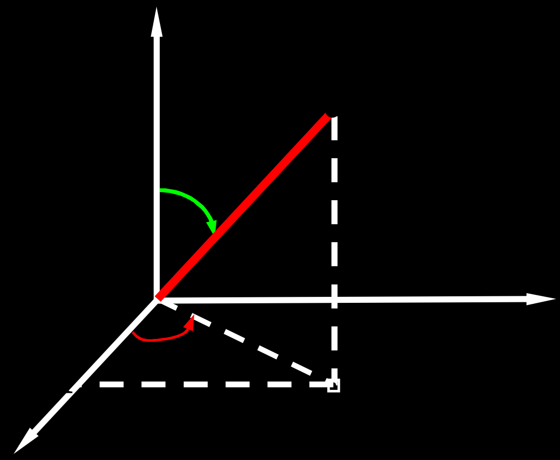
But for associated Legendre function $P^m{}_l$:

is not, in general, a polynomial——if m is odd it carries a factor of

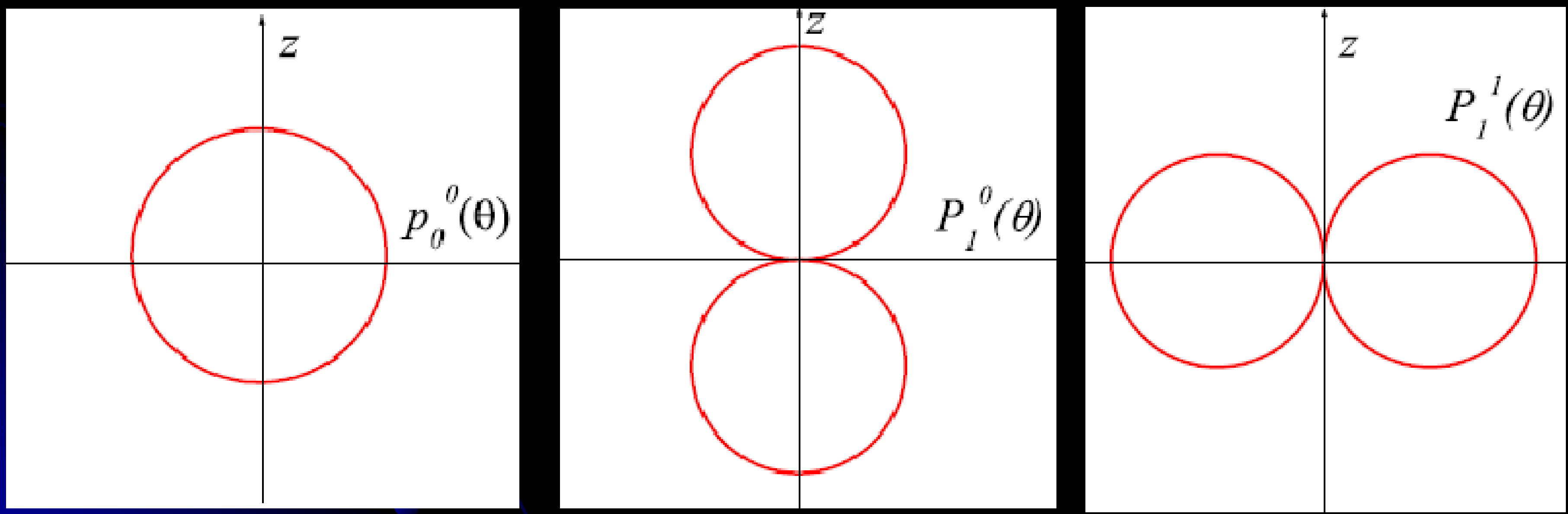
not a polynomial

$P_2^2(x)$

As



Plot:



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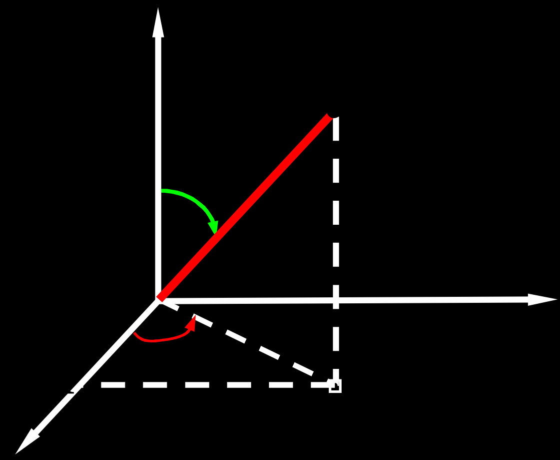
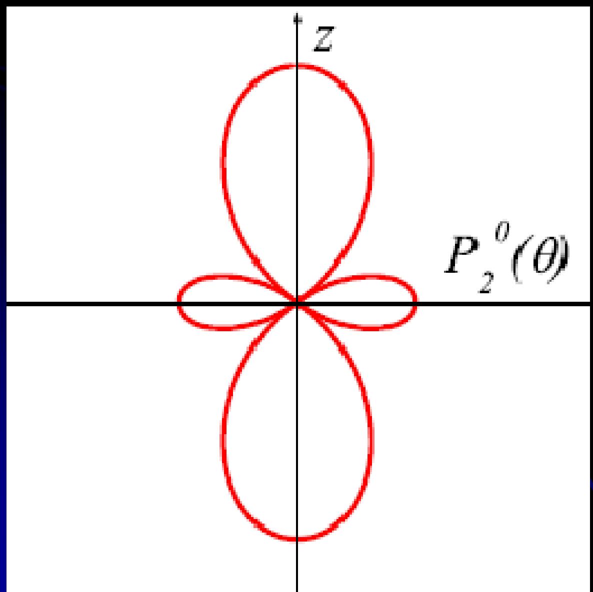
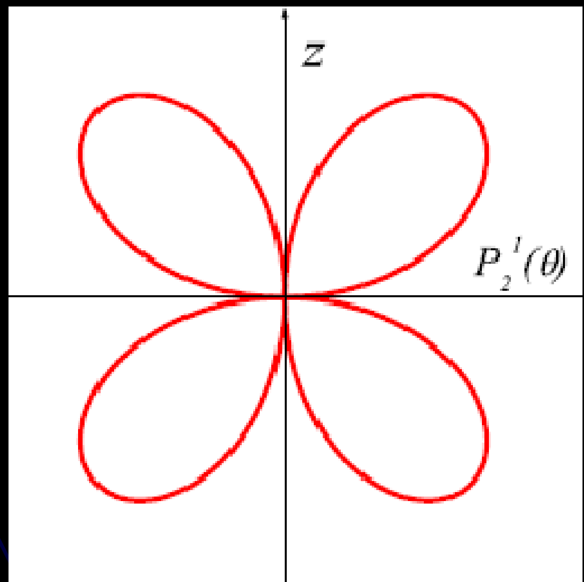
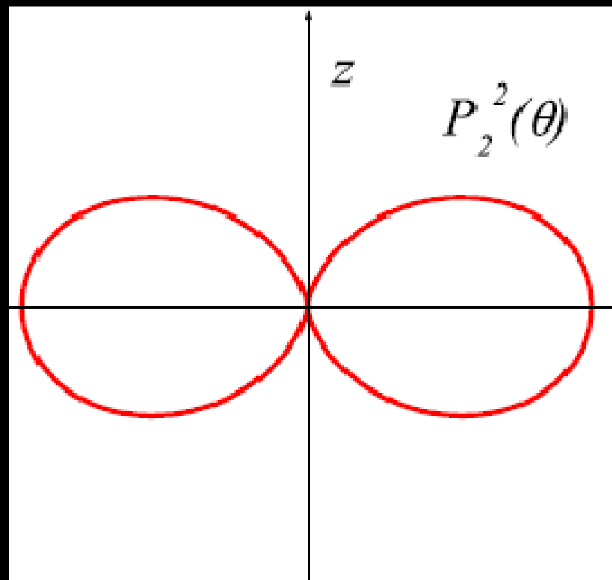
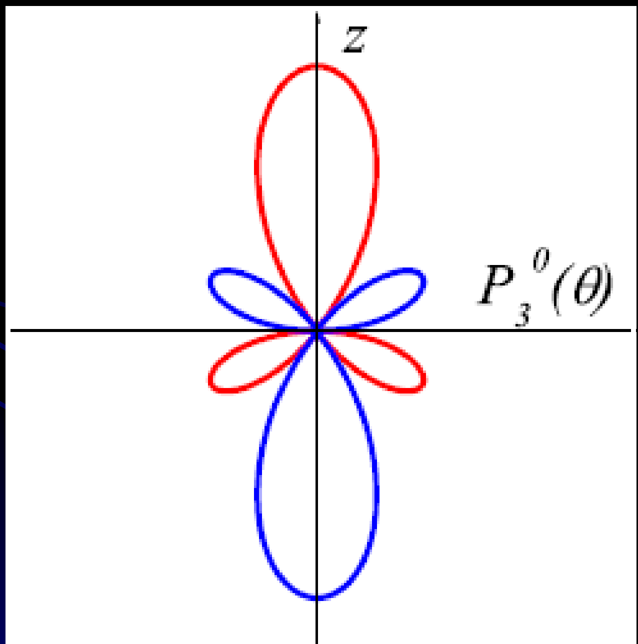


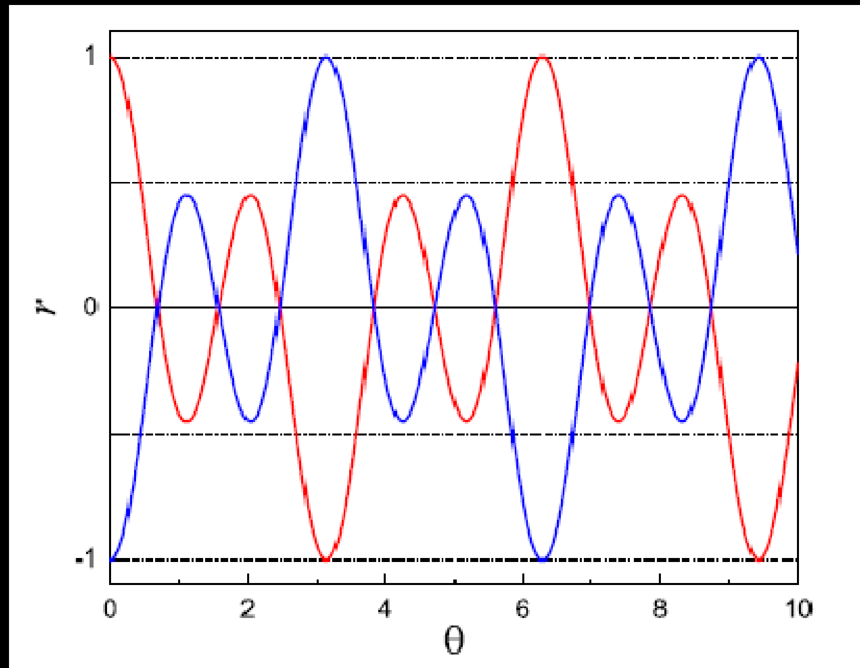






Plot:





$r(\theta)=\frac{1}{2}(5\cos$

Some Notes:

(1) Notice that l must be a nonnegative *integer*, for the Rodrigues formula to make any sense.

If $|m|>l$, then $P_l^m=0$. Therefore, for any given l, there are $(2l+1)$ possible values of m:

(2) Now, the volume element in spherical coordinates is

so the normalization condition becomes

It is convenient to normalize R and Y separately:

where ***R*** determined by ***V(r)*** and Y can be obtained.

The normalized angular wave functions are called ***spherical harmonics***:

where

Now we list here some few spherical harmonics: See book for more

Notice that

Actually, the *Y*s are automatically orthogonal, so

For historical reasons, *l* is called the azimuthal quantum number, and *m* the magnetic quantum number.

4.1.3 The Radial Equation

Notice that the angular part of the wave function, $Y(\theta,\Phi)$, is the same for all spherically symmetric potentials; the actual shape of the potential, $V(r)$, affects only the radial part of the wave function, $R(r)$, which is determined by Equation 4.16:

This equation can be simplified if we change variables as

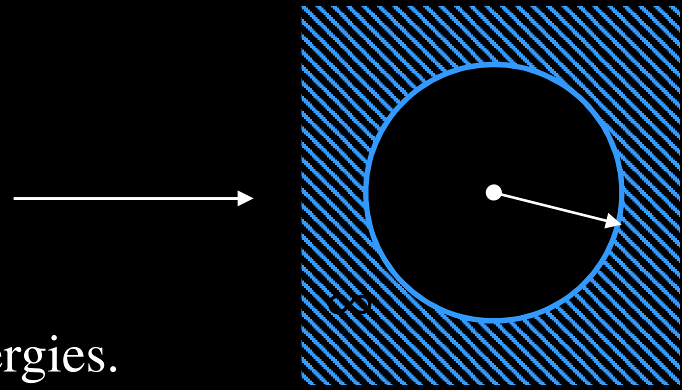
so that

and hence

This is called the radial equation; it is *identical in form* to the one-dimensional Schrödinger Equation , except that the effective potential,

contains an extra piece, the so-called centrifugal term, . It tends to throw the particle outward (away from the origin), just like the centrifugal (pseudo-) force in classical mechanics. Meanwhile, the normalization condition becomes

The ***infinite spherical well***:



Find the wave function and the allowed energies.

Solution:

1. Outside the well, the wave function is zero: $u(r, r=a \text{ or } r>a)=0$.

2. Inside the well, the radial equation reads

where

(1) The case $l=0$ is easy:

Then the solution is

As the second term blows up, so we must choose *B=0*.

The boundary condition then requires that

The allowed energies are evidently

which is the same for the one-dimensional infinite square well.

The normalization condition:

yields

Tacking on the angular part ($l=0, m=0$)

we conclude that

Notice that the stationary states are labeled by three quantum number, n, l and m: ψ_{nlm}. The energy, however, depends only on n and l: E_{nl}.

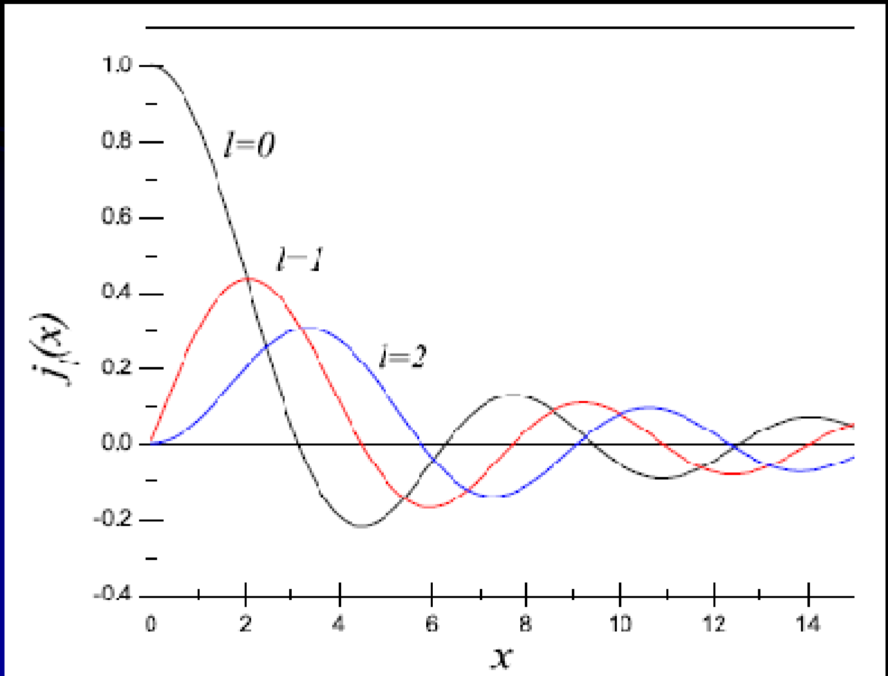
(2) The case l is in any integer:

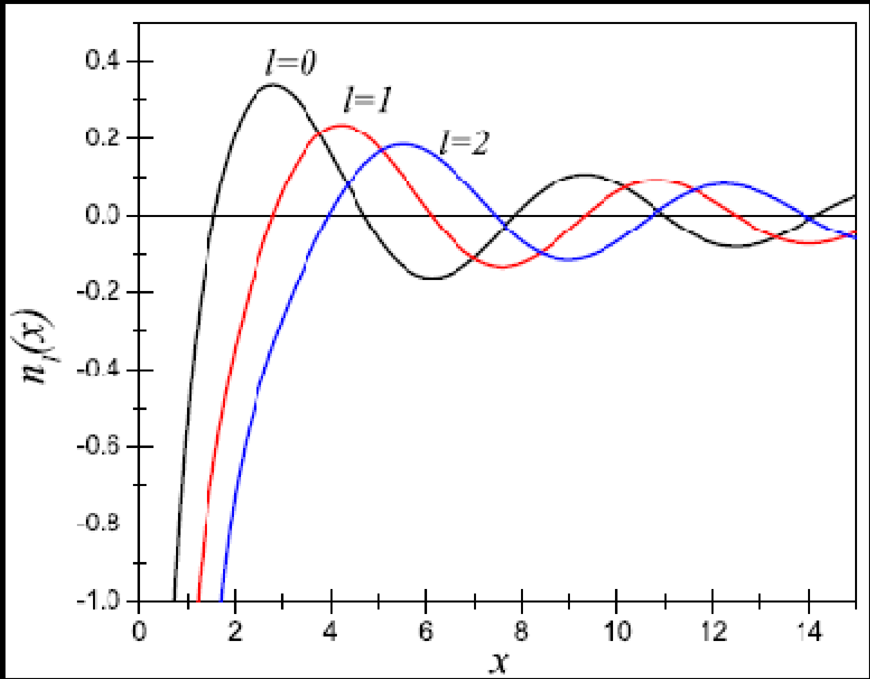
The general solution of above equation is:

where $j_l(kr)$ is the spherical *Bessel function* of order l, and $n_l(kr)$ is the spherical *Neumann function* of order l. They are defined as follows:

Spherical *Bessel function:*

Spherical *Neumann function*





The asymptotic properties of two functions :

Generally, for small *x*, we have

Proof: For small *x*,

As when $x \to 0$, *Neumann functions* blow up, that is

in the general solution, we must set $B=0$,

and hence

The boundary condition then requires that $R(a)=0$. Evidently k must be chosen such that

that is, (ka) is a zero of the lth-order spherical Bessel function. Now, the Bessel functions are oscillatory; each one has an infinite number of zeros. However, unfortunately for us, they are not regularly located and must be computed numerically. At any rate, if we suppose that the boundary condition requires that

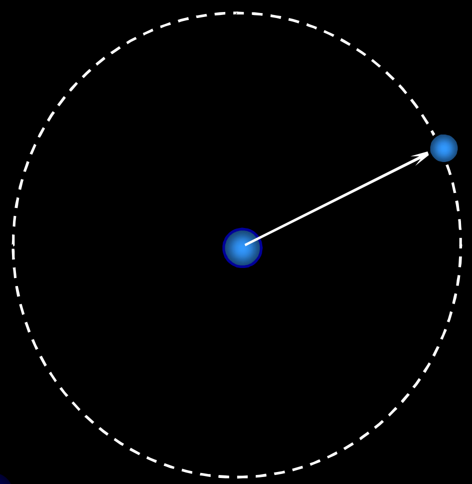
where β_{nl} is the nth zero of the lth spherical Bessel function. The allowed energies, then, are given by

and the wave functions are

with the constant A_{nl} to be determined by normalization. Each energy level is $(2l+1)$-fold degenerate, since there are different values of m for each value of l.

4.2 The Hydrogen Atom

The hydrogen atom consists of a heavy, essentially motionless proton, of charge e, together with a much lighter electron (charge $-e$) that orbits around it, bound by the mutual attraction of opposite charges.



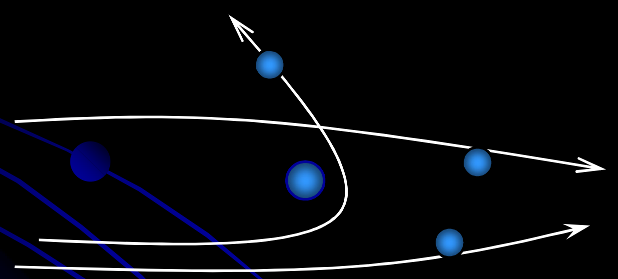
From Coulomb's law, the potential energy (in SI units) is

Then the radial equation for hydrogen atom says

Our problem is to solve this equation for *u(r)*, and determine the allowed energies, *E*. Now we consider this problem in detail by using analytical method.

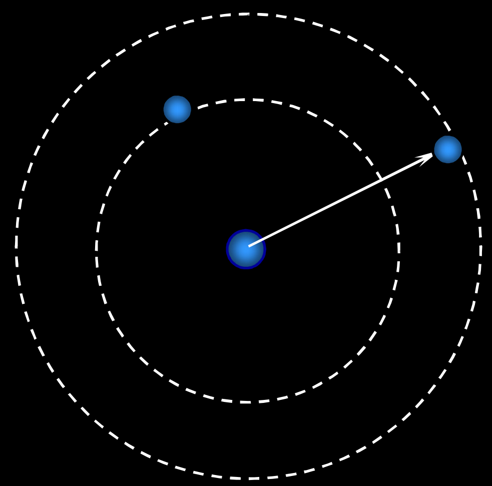
Incidentally, Coulomb potential, admits two different states,

continuous states and *bound* states, which are separately corresponds to the following situations:



continuous states *E>0,*

describing electron-proton scattering



bound states *E<0*,

representing Hydrogen atom

4.2.1 The Radial Wave Function

1. Radial Solution:

The radial equation for Hydrogen atom is

$(E<0)$

(1) Simplify it (tidy up):

As $E<0$, then we let

Dividing above equation by E, we have

This suggests that we introduce

So that

(2) The asymptotic properties of the solution:

In this case, the constant term in the bracket of above equation dominates, so (approximately)

The general solution of it is

but the second term blows up as , so *B=0*. Evidently,

for large .

In this case, the *centrifugal* term dominates; approximately, then:

The general solution of it is

But for $\rho \rightarrow 0$, the term ρ^{-l} blows up, so $D=0$. Thus

for small .

(3) Introduce new function $v(\rho)$ to simplify solution:

The next step is to peel off the *asymptotic* behavior, introducing the new function $v(\rho)$:

in the hope that $v(\rho)$ will turn out to be simpler than $u(\rho)$. Then

In terms of $v(\rho)$, then, the radial equation of $u(\rho)$ reads

[4.61]

(4) Solve above equation by power series method:

Finally, we assume the solution, $v(\rho)$, can be expressed as a power series in ρ:

Now replace $v(\rho)$ into equation and our problem is to determine the coefficients of the series, $c_1, c_2, c_3, \ldots$. Differentiating term by term:

Differentiating again,

Inserting these into Equation 4.61, we have

where

Equating the coefficient of like powers yields

or:

This recursion formula determines the coefficients, and hence the function $v(\rho)$: We start with c_0, and recursion formula gives us c_1; putting this back in, we obtain c_2, and so on.

At last, after c_0 being fixed eventually by normalization, the solution of $v(\rho)$ and $u(\rho)$ will be got.

2. Energies of the solutions:

If j is very large, that is $j \rightarrow \infty$, the recursion formula says

Then

so

and hence

which blows up at large $\rho \rightarrow \infty$ and is not permitted because the solution will not be properly normalized. In order to satisfy the normalization condition, there is only one way out of this dilemma: *The series must terminate*. There must occur some maximal integer, j_{max}, such that

Evidently, from recursion formula

we get

Defining , which is the so-called ***principle quantum number***,
we have

so the allowed energies are

This is the famous ***Bohr formula*** ——by any measure the most important result in all of quantum mechanics. Bohr obtained it in 1913 by a serendipitous mixture of inapplicable classical physics and premature quantum theory.

And we also find that

where

$a =$

is the so-called ***Bohr radius***.

It follows that

3. The overall solutions of Hydrogen atom:

Finally, the spatial wave functions of hydrogen are labeled by three quantum numbers (*n,l, and m*):

where

and $v(\rho)$ is a polynomial of degree $j_{max} = n\text{-}l\text{-}1$ in ρ, whose coefficients are determined by the recursion formula

(1) The ground state:

The ground state (that is, the state of lowest energy) is the case $n=1$; putting in the accepted values for the physical constants, we get

Evidently the *binding energy* of hydrogen (the amount of energy you would have to impart to the electron in the ground state in order to ionize the atom) is *13.6 eV*. As the principle quantum number $n=1=j_{max}+l+1$, the angular quantum number must be zero ($l=0$), whence also $m=0$, so the wave function is

$R_{nl}(r)$

Normalizing R_{10} by

we have

Meanwhile, $Y_0^0=$, and hence the ground state of hydrogen is

(2) The first excited states $n=2$:

If $n=2$ the energy is

This is the first excited states, since we can have either $l=0$ (in which case $m=0$) or $l=1$ (in which case $m=-1, 0,$ or 1); Evidently there are four states that share the same energy E_2.

If $l=0$, the recursion relation gives

so

and therefore

Normalization

If $l=1$,

the recursion formula terminates the series after a single term;

and we find

Normalization

R_{nl}

(3) The excited states for arbitrary n:

For arbitrary n, the possible values of l are

and for each l there are ($2l+1$) possible values of m, so the total degeneracy of the energy level E_n is

The polynomial $v(\rho)$ (defined by the recursion formula Eq.4.76 is a function well known to applied mathematicians; apart from normalization, it can be written as

where

is the ***associated Laguerre polynomial***, and

is the *q*th ***Laguerre polynomial***.

Therefore the radial wave function is

Examples:

$R_{10}(r) =$

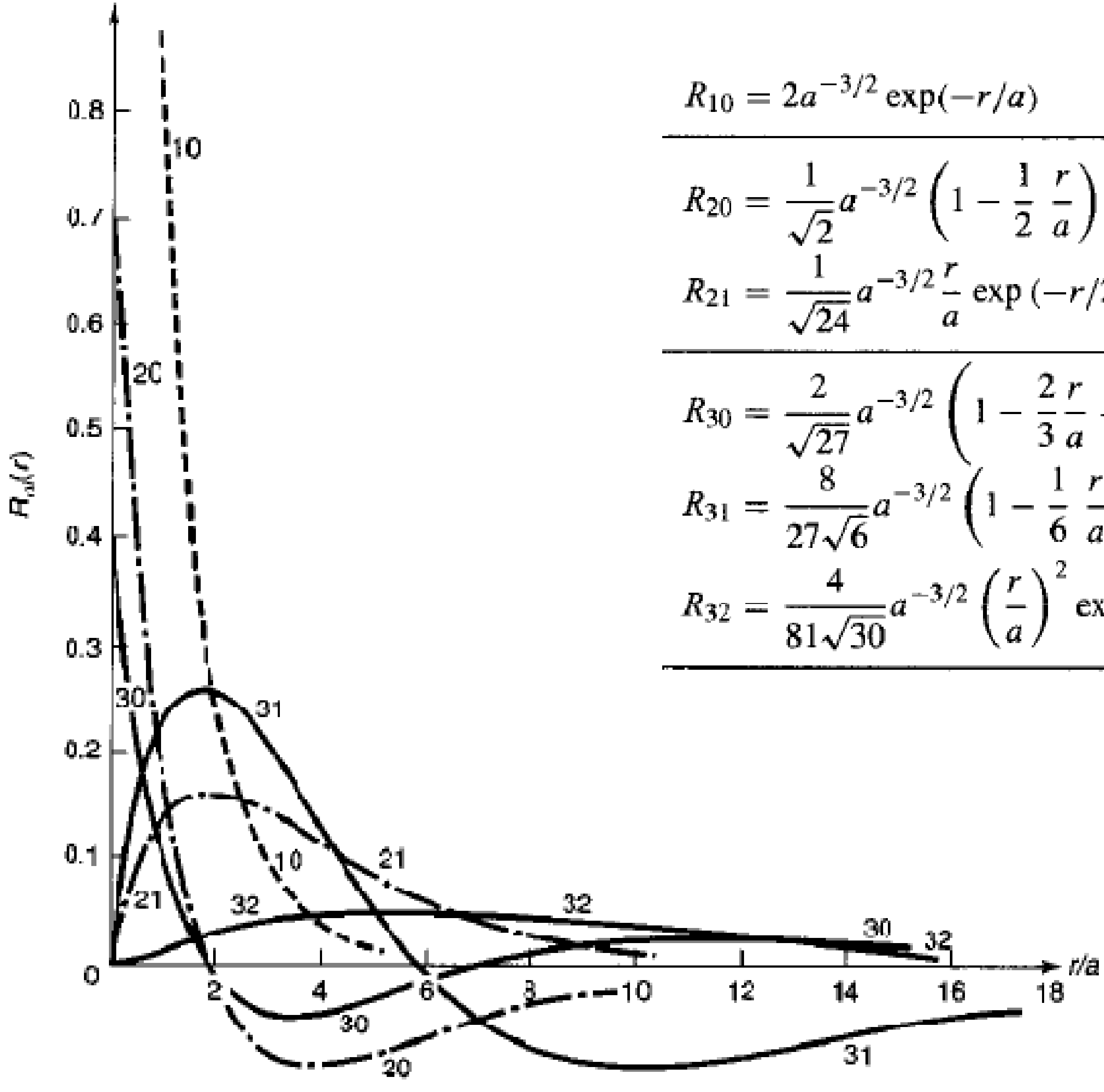
Normalization

Normalization

Generally, we can normalize R_{nl} as

to give normalized R_{nl} as follows

with normalization constant N_{nl} being



$$R_{10} = 2a^{-3/2}\exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)\exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}\exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}}a^{-3/2}\left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right)\exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)\exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2}\left(\frac{r}{a}\right)^2\exp(-r/3a)$$

Figure 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

Then, finally, the normalized hydrogen wave function are

Notice that whereas the wave functions depend on all three quantum numbers, the energies are determined by n alone. This is a peculiarity of the Coulomb potential; generally, the energies depend also on l.

The wave functions are mutually orthogonal

Visualizing the hydrogen wave functions is not easy. See book!

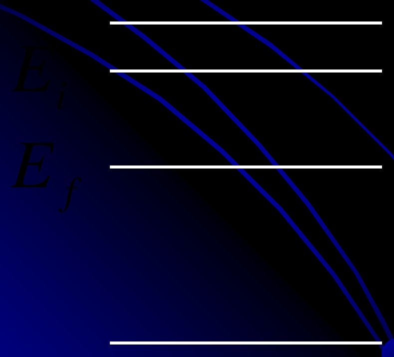
See the figures of solutions of

Hydrogen atom

4.2.2 The Spectrum of Hydrogen

In principle, if you put a hydrogen atom into some stationary state ψ_{nlm}, it should stay there forever. However, if you *tickle* it slightly (by collision with another atom, say, or by shining light on it), the electron may undergo a ***transition*** to some other stationary state——either by *absorbing* energy, and moving up to a higher-energy state, or by *giving off* energy (typically in the form of electromagnetic radiation), and moving down.

In practice such *perturbations* are always present; transitions (or, as they are sometimes called, "*quantum jumps* ") are constantly occurring, and the result is that a container of hydrogen gives off light (*photons*), whose energy corresponds to the difference in energy between the initial and final states:



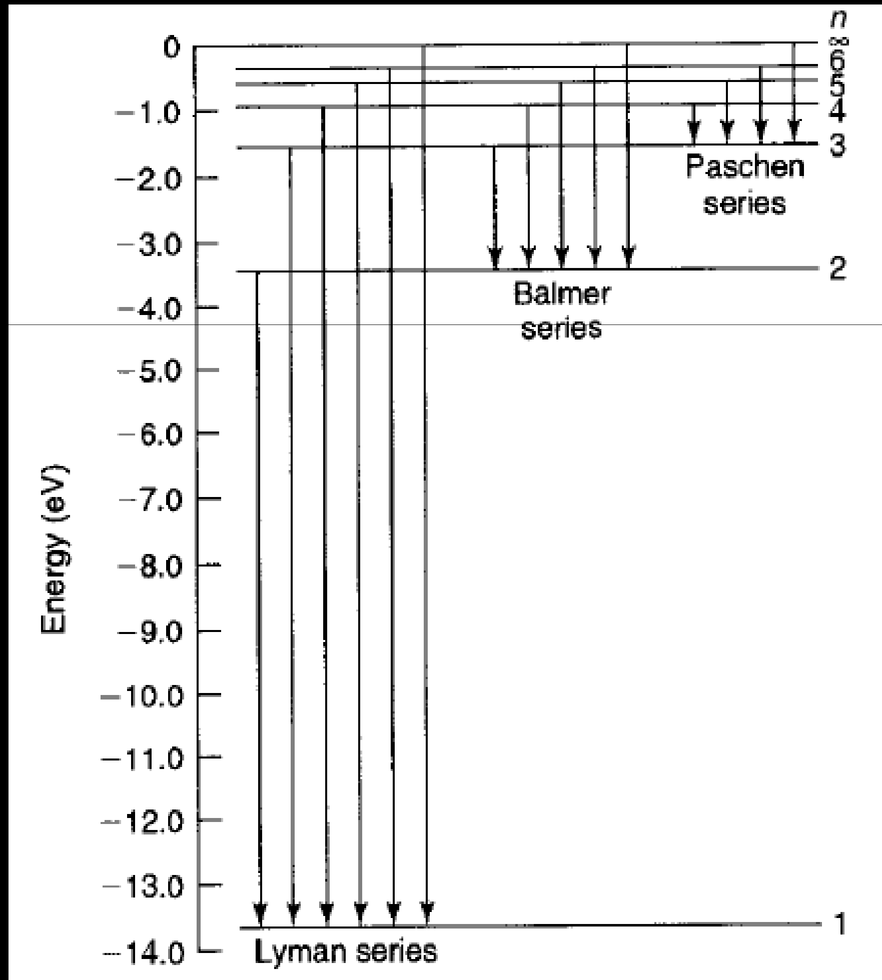
Now according to the ***Planck formula***, the energy of a photon is proportional to its frequency:

Meanwhile, the *wavelength* is given by , so

where

is known as the *Rydberg constant*. Above equation is the *Rydberg formula* for the spectrum of hydrogen; it was discovered empirically in 19th century, and the greatest triumph of Bohr's theory was its ability to account for this result——and to calculate R in terms of the fundamental constants of nature.

Spectrum of Hydrogen:



Transitions to the ground state (n_f=1) lie in the ultraviolet; they are known to spectroscopists as the *Lyman series*.

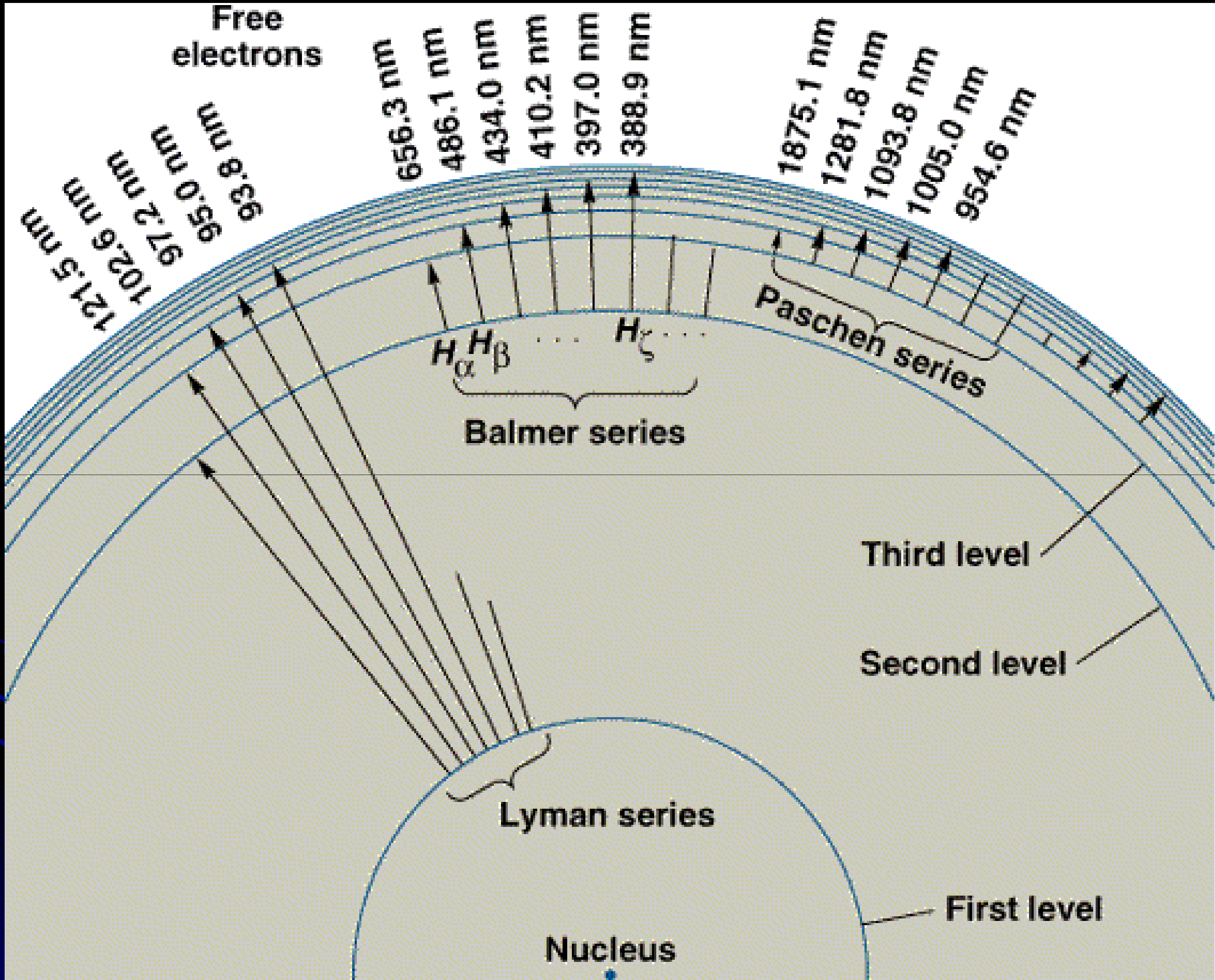
莱曼系

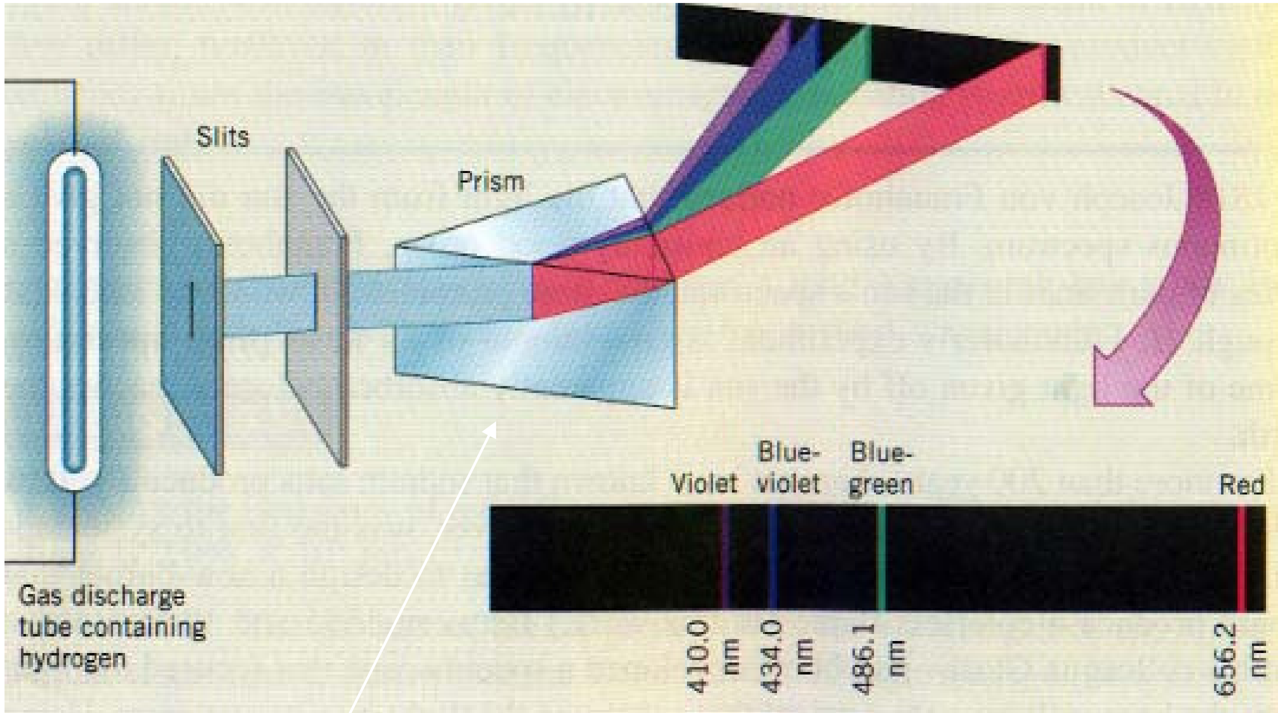
Transitions to the first excited state (n_f=2) fall in the visible region; they constitute *Balmer series*.

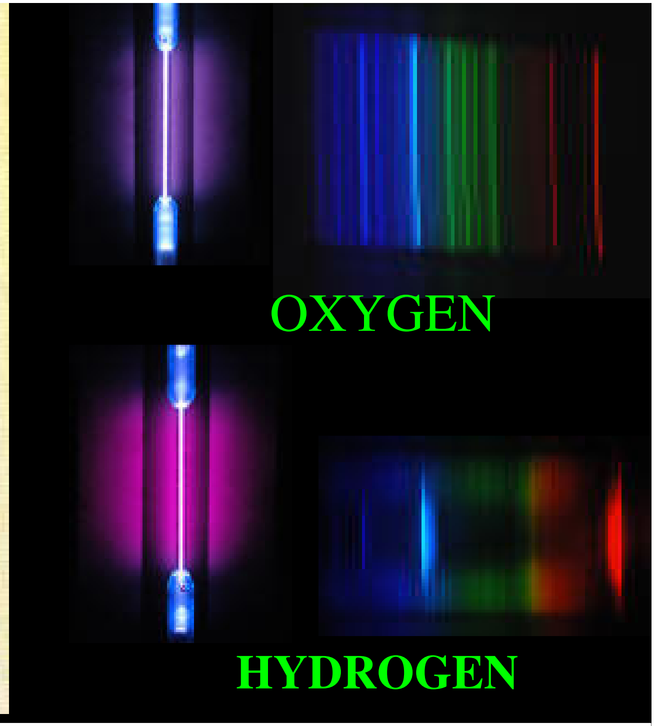
巴尔末系

Transitions to n_f=3 (*Paschen series*) are in the infrared region; and so on.

帕刑系

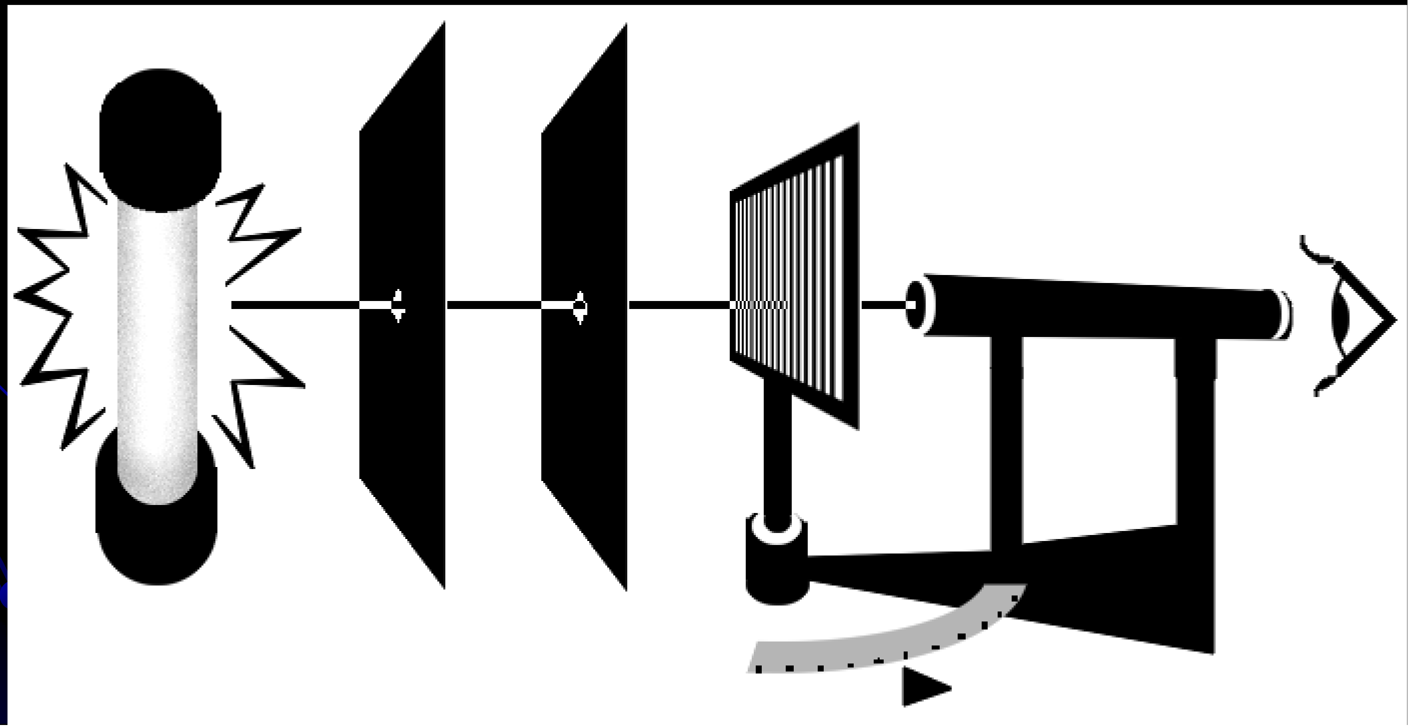

Free
electrons
121.5 nm
102.6 nm
97.2 nm
95.0 nm
93.8 nm
656.3 nm
486.1 nm
434.0 nm
410.2 nm
397.0 nm
388.9 nm
1875.1 nm
1281.8 nm
1093.8 nm
1005.0 nm
954.6 nm
H_α H_β . . . H_ζ . . .
Balmer series
Paschen series
Third level
Second level
Lyman series
First level
Nucleus

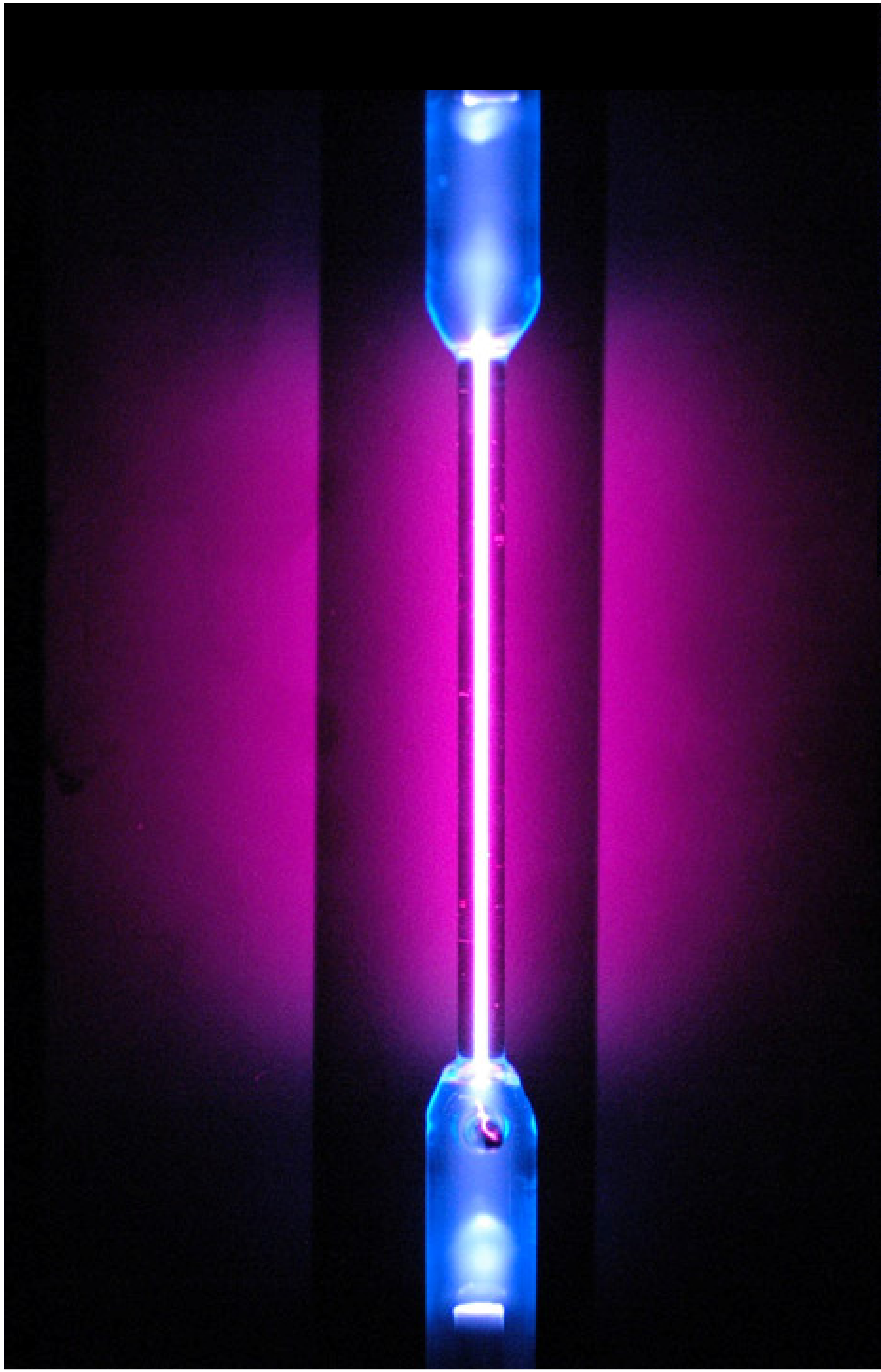


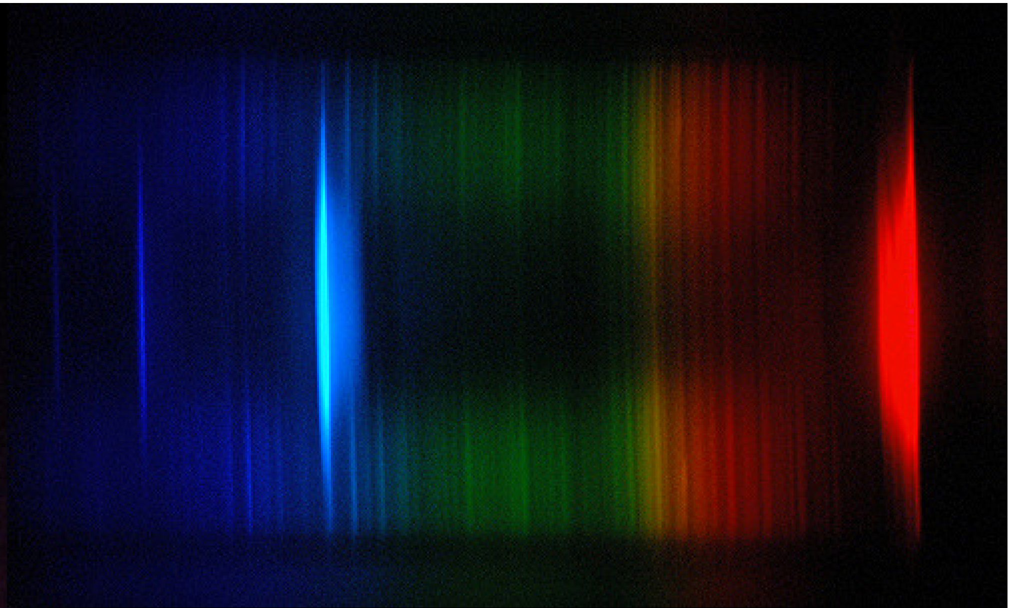


prism

diffraction grating







These spectral lines are produces by "exciting" gas atoms and molecules with high voltage (about 5000 volts). This energy kicks electrons to higher energy levels where they are unstable and drop back towards the ground state (lower energy levels). As the electrons make this downward transition, they release energy in the form of visible light.

The emission and absorption spectrum of hydrogen in the visible range is the following

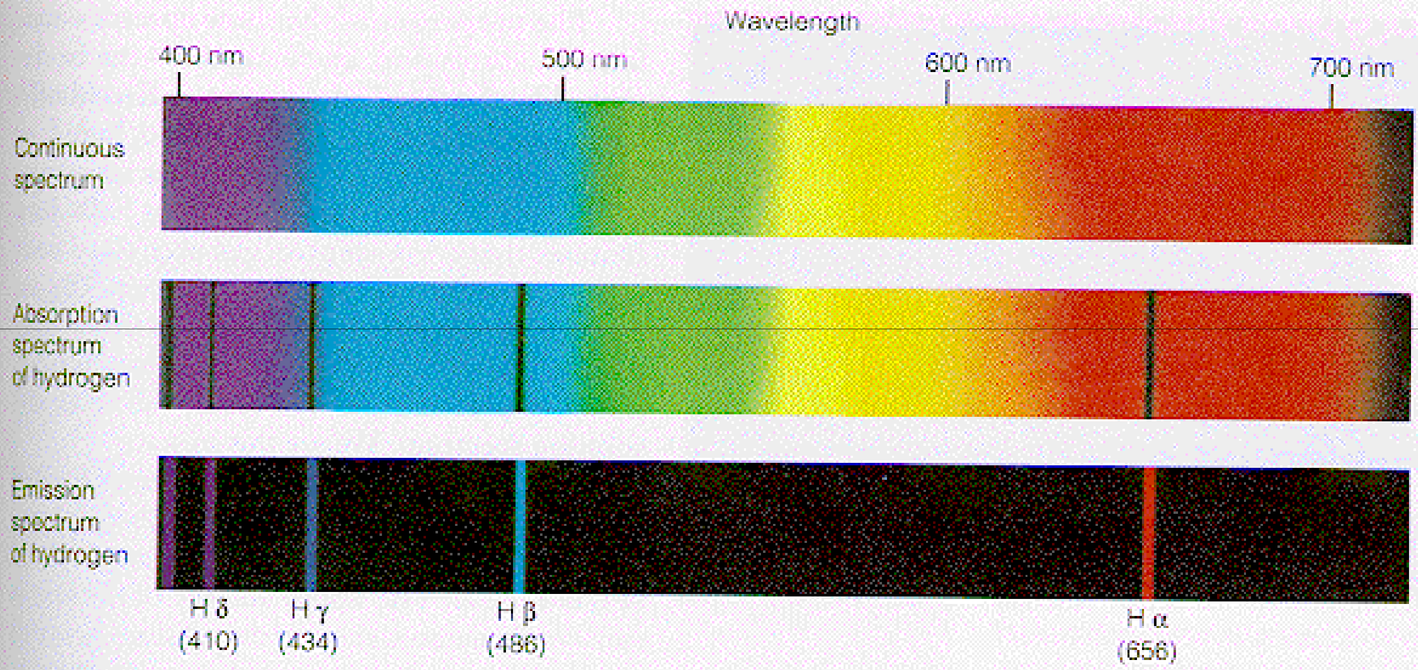
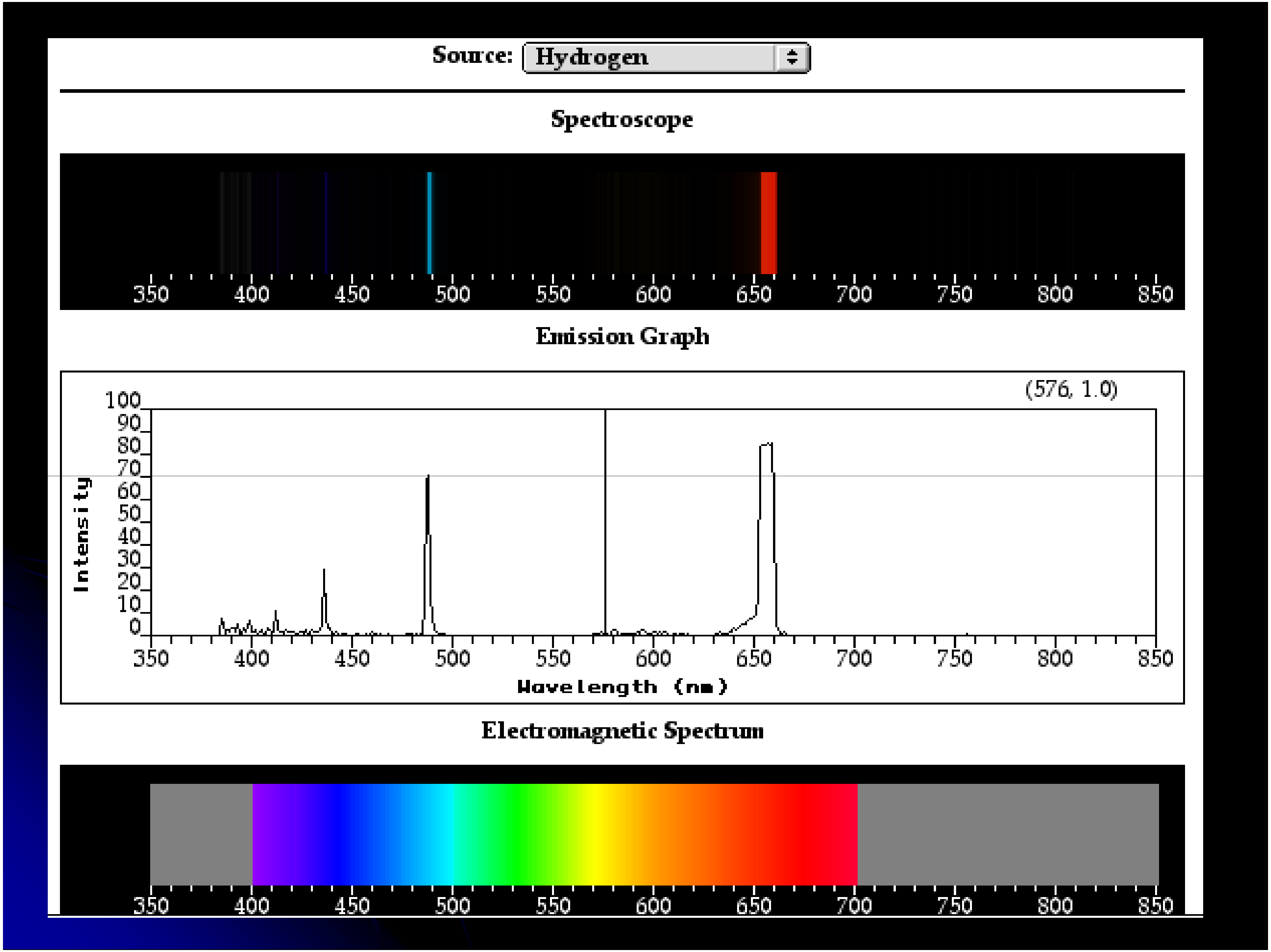


FIGURE 6-7
The three types of spectra. A continuous spectrum (top) contains no bright or dark lines, but an absorption spectrum (middle) is interrupted by dark absorption lines. An emission spectrum (bottom) is dark except at certain wavelengths where emission lines occur. Note that the lines in the absorption spectrum of hydrogen have the same wavelength as the lines in the emission spectrum of hydrogen.



Source:
Hydrogen
Spectroscope
Emission Graph
(576, 1.0)
Intensity
Wavelength (nm)
Electromagnetic Spectrum

End