Quantum Physics – particle confinement and quantisation of energy

Text: Walker *etal. (2021), Halliday's Fundamentals of Physics – First Australian and New Zealand Edition* John Wiley & Sons Australia (HW)

With many thanks to Walter Kalceff for the use of his original lecture notes.

Imagine you were studying physics (natural philosophy) before Newton

- There were lots of experiments with results and *partial* explanations
    - Pendulum motion
    - Falling bodies
    - Bodies on inclined planes
    - Planetary motion
- But there was no unifying theory, and no way to predict results of new experiments

- Newton's laws provided this theory!

- So is there a unifying theory that allows us to predict and explain all the weird quantum experiments?

Quantum Mechanics and Schrödinger's equation

(or $W (= Fx) = \Delta K$ etc)

Schrödinger's equation replaces $\vec{F} = m\vec{a}$ for the motion of particles on an atomic scale.

It must satisfy the wave equation, since the particles have wave properties.

- But what is the dependent variable?
  - E.g. for an EM wave, the dependent vars are E and B strength, for a sound wave it is pressure

- The dependent variable is the wave function Ψ (Psi)

- The square of its magnitude has physical significance – the probability of the particle being there (between *x* and *x+dx*)!

$$\boxed{Prob \propto |\Psi|^2 \Delta x}$$

So you can at best know *probably* where a particle is located. But since you've already come to peace with the fact that you can't know a particle's position and momentum to a high level of precision, you're probably okay with this concept too ☺

How to use Schrödinger's equation

- Use it to calculate Ψ
- Then from Ψ calculate the interesting properties of the electron's motion, like KE, etc.
- Also, the probability the electron will arrive at a certain position *x*, $|\Psi|^2 dx$.

- Ψ is a construct and used like $\vec{\mathrm{E}}$ in EMag theory
- You can it to predict interference patterns etc, but you only experimentally measure $\left|\vec{\mathrm{E}}\right|^2$

One dimensional SE for electron for a potential energy that depends only on *x* not *t*

$$\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + \big(E - U(x)\big)\psi = 0$$

Wave function that only depends on *x*

Total E

PE e.g. from Coulomb F

You don't have to use the SE yourself, this is just important background theory to help you understand the effects we will soon be predicting

The free electron and Schrödinger's equation

One dimensional SE for electron for a potential energy that depends only on *x* not *t*

$$\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + \big(E - U(x)\big)\psi = 0$$

Such an electron has all its E in form of KE

Let our electron travel in a region of constant potential E

- let U=0 for simplicity
- It is isolated (doesn't interact with anything) so total energy is a constant.

$$\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + E\psi = 0$$

Look closely – this has the same form as the pendulum or LC circuit equations!

$$\psi = A\sin\frac{2\pi}{h}\sqrt{2mE}x + B\cos\frac{2\pi}{h}\sqrt{2mE}\,x$$

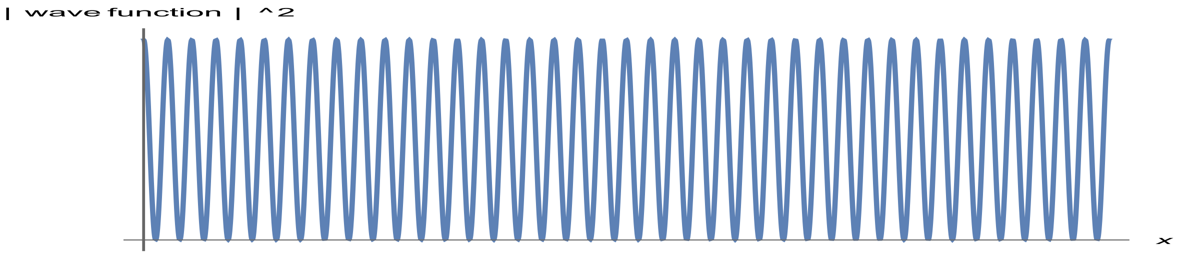
$$= A\sin\frac{2\pi}{\lambda}x + B\cos\frac{2\pi}{\lambda}x$$

$$\lambda = \frac{h}{\sqrt{2mE}}$$

The free electron and Schrödinger's equation

$$\psi = A\sin\frac{2\pi}{h}\sqrt{2mE}x + B\cos\frac{2\pi}{h}\sqrt{2mE}\,x$$
$$= A\sin\frac{2\pi}{\lambda}x + B\cos\frac{2\pi}{\lambda}x$$

Understand what this wave function means in terms of the behaviour of the e-



- This is an **infinitely** long train of waves
- It has a **precise** wavelength and momentum

$$\lambda = \frac{h}{\sqrt{2mE}} \text{ and } p = \frac{h}{\lambda}$$

- A precise *p* means a completely imprecise *x*, which is why the wave train is so long.
  $(\Delta p = 0)$ $(\Delta x = \infty)$

- But **if** we know (sort of) where the e- is, the wave is different:
- It's a wave packet! Its small so Δp becomes big, and it travels at $v = \sqrt{\frac{2K}{m}}$

The free electron

A free electron has a kinetic energy of 10 eV.

Find its corresponding speed.

If the speed is known to 1.0% accuracy, what is the accuracy with which we can measure the electron's position?

v=1.9x10^{6} m/s; Δx=40 nm or 6nm using h/2pi

The free golf ball

A golf ball has a mass of 45 g and speed of 75 m/s measured to 1.0% accuracy.

What is the accuracy with which we can measure its position?

Δx=2x10^{-32} m <<< smaller than an atom!

String Waves and Matter Waves

- Confinement of a wave leads to quantisation – that is, to the existence of discrete states with discrete wavelengths. The wave can only have those wavelengths.

- This observation applies to waves of all kinds, including matter waves. For matter waves, however, we will deal with the energy, *E,* of the wave packet and not the frequency *f*, which has no physical significance.

Energies of trapped electron : - one dimensional trap

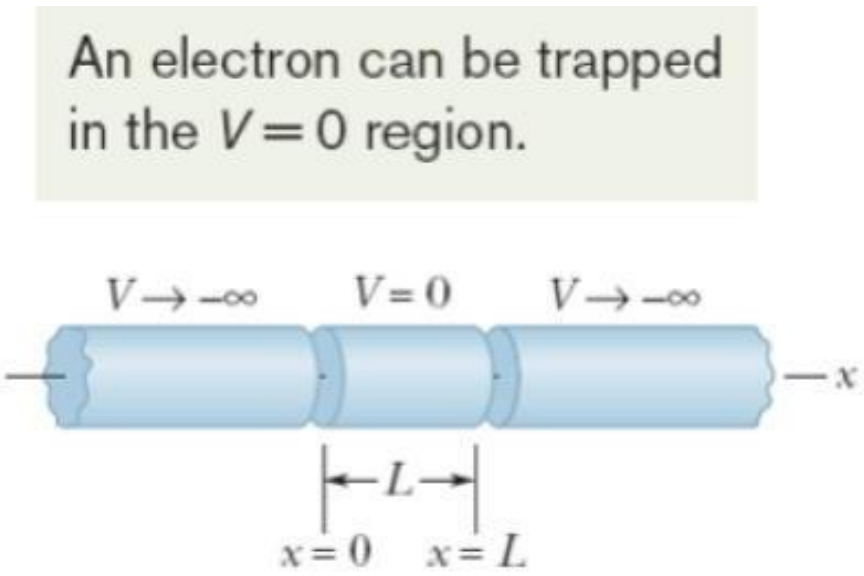


Fig. 39-1 The elements of an idealized "trap" designed to confine an electron to the central cylinder. We take the semi-infinitely long end cylinders to be at an infinitely great negative potential and the central cylinder to be at zero potential.

$$L = \frac{n\lambda}{2}, \qquad for\ n = 1, 2, 3, \ldots ..$$

Each value of *n* identifies the state of the oscillating string; the integer *n* is a **quantum number**.

For each state of the string, the transverse displacement of the string at any position *x* along the string is given by:

$$y_n(x) = A \sin\left(\frac{n\pi}{L} x\right),$$

for n = 1, 2, 3, ……

Trapped electron: - finding quantised energies

An electron can be trapped in the $U = 0$ region.

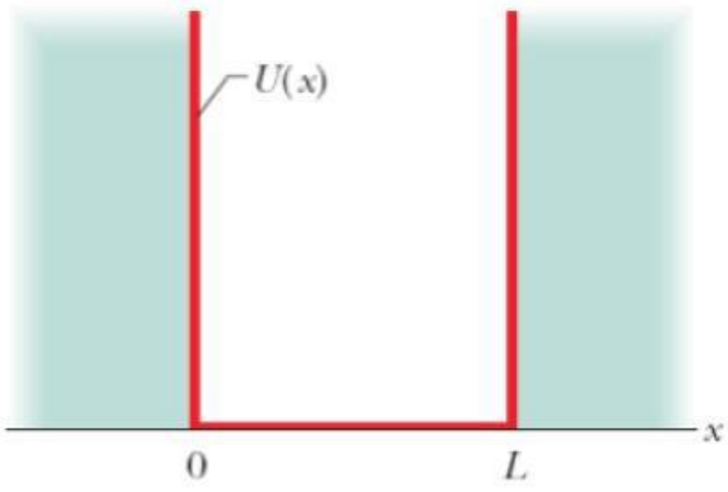
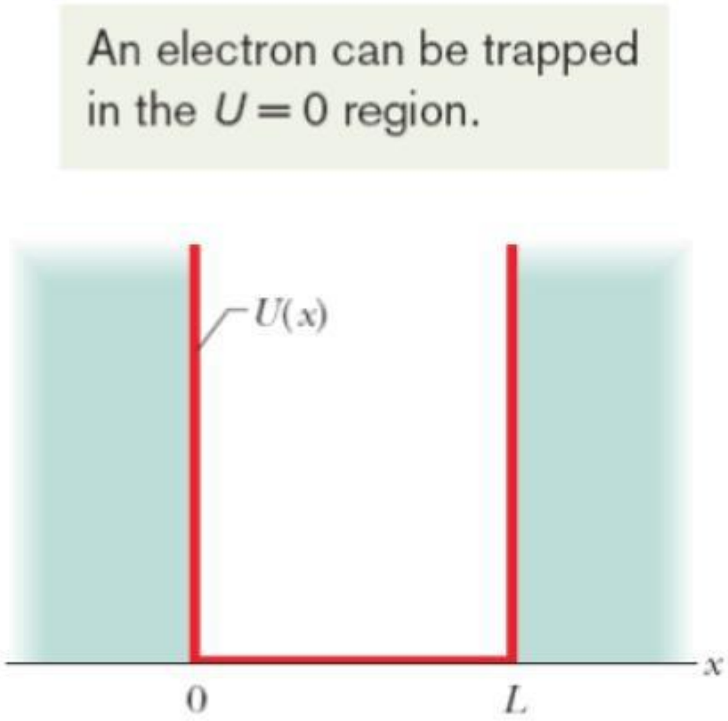


Fig. 39-2 The electric potential energy $U(x)$ of an electron confined to the central cylinder of the idealized trap of Fig. 39-1. We see that $U = 0$ for $0 < x < L$, and $U \to \infty$ for $x < 0$ and $x > L$.

In the region 0 to L the electron's potential energy is zero as V=0. Outside this 'well' its energy would be positive and infinite in magnitude as V goes to infinity. This potential pattern is called an **infinitely deep potential energy well** as an electron trapped in it cannot escape.

It reflects from each wall due to a force of essentially infinite magnitude.

Trapped electron: - finding quantised energies using the SE



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Want to use the Schrödinger equation? Here's how:

First, just look at the region of 0<*x*<*L* where *U* = 0. Subs that into the SE

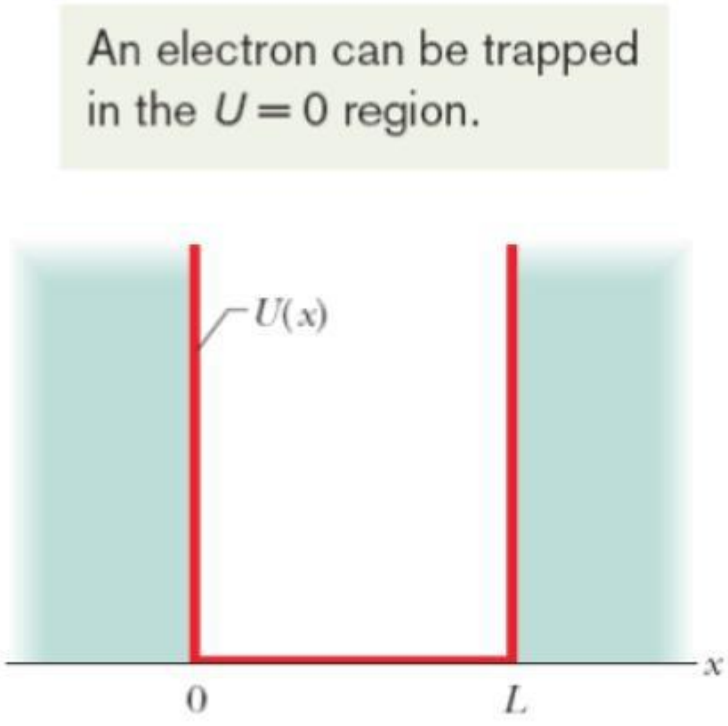
$$\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + E\psi = 0$$

As before, this has a solution of a sinusoidal wave.

But now! The probability of finding the e- outside the well is zero ($|\psi|^2 = 0$).
The solution of ψ has to be 0 when $x \geq 0$ and $x \leq L$.

Trapped electron: - finding quantised energies

Interference of de Broglie waves!



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Like a standing wave in a string, the matter wave describing the trapped electron must have nodes at $x = 0$ and $x = L$.

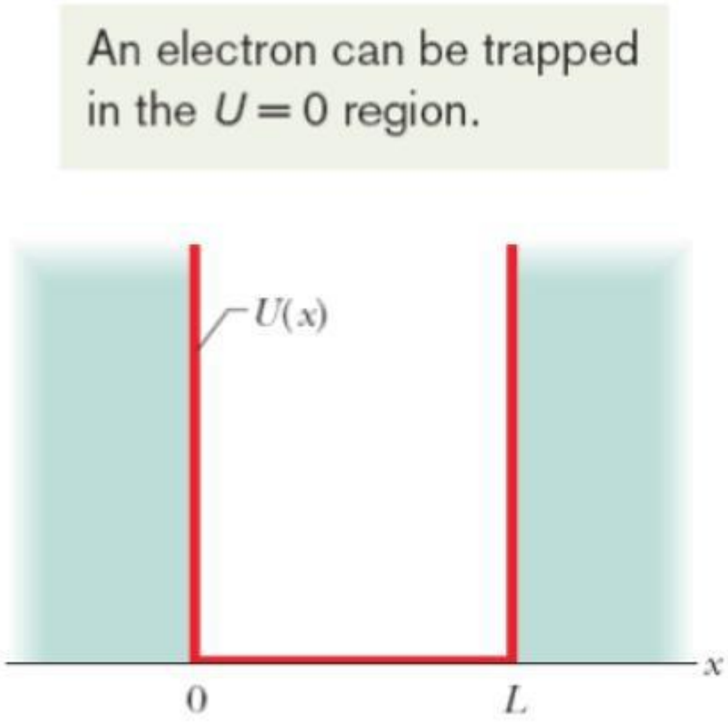
This determines the allowed e- wave packet wavelengths.

This is turn determines the allowed e- momenta and energies:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK}}$$

Know the allowed standing wave patterns and their wavelengths, momenta, and energies

Trapped electron: - finding quantised energies



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Substituting into $L = \frac{n\lambda}{2}$ and solving for *E* we get for a one dimensional infinite well of width *L*:

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2 \qquad \text{for } n = 1, 2, 3, \dots \dots$$

The trapped e- can only have an energy from a set of discrete values!

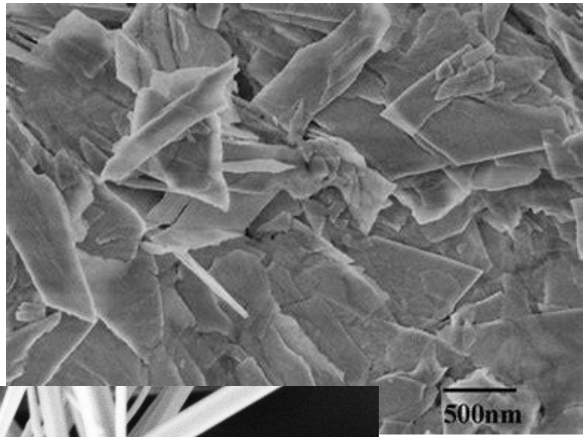
This can be extended to two and three dimension with:

$$E_{n_x x, n_y y, n_z y} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

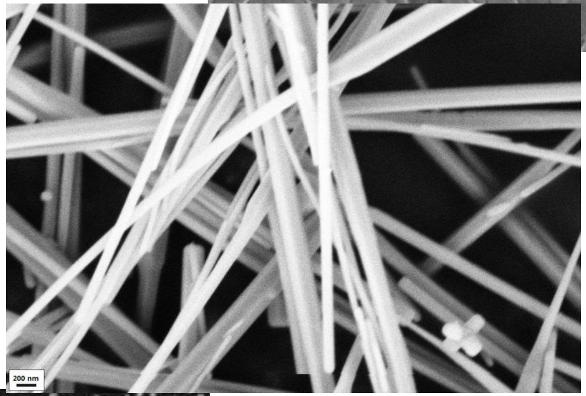
The *n*'s are called quantum numbers
The allowed *E*'s are called energy levels

What can these wells look like?

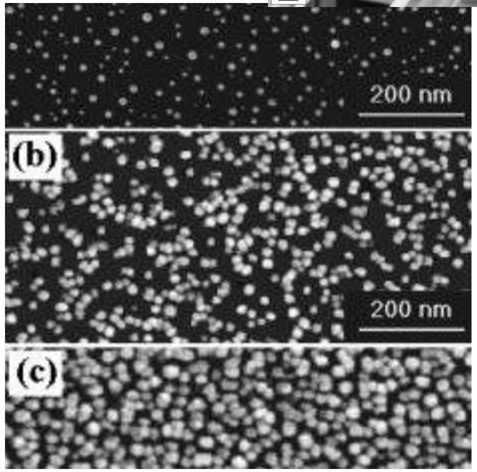
1-D confinement (free to move in 2D)



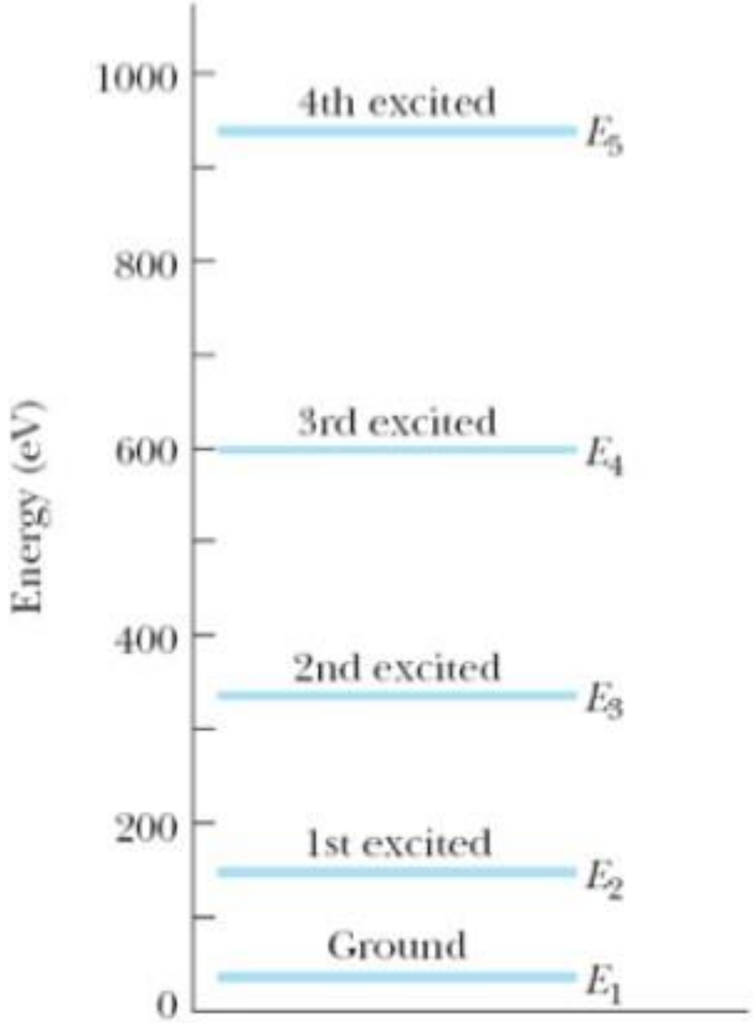
2-D confinement (free to move in 1D)
= quantum wire



3-D confinement (not free to move)
= quantum dot



Trapped electron: - finding quantised energies



The diagram to the left is Figure 39-3 from the textbook and shows the lowest five allowed energy values for an infinite well of L = 100 pm. These are called **energy levels**. A wave packet described by wave function with a certain n value is in **quantum state** n.

n = 1 is the ground state and has the lowest possible energy where the electron tends to reside. For n > 1, the electron is said to be in an excited state with n = 2 the first excited state.

Zero Point Energy

In the result

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2 \qquad \text{for } n = 1, 2, 3, \dots\dots$$

n = 1 is the quantum state with lowest energy for an electron in an infinite potential well, the **ground state**.

The energy of an e- in the ground state is $E_1 \neq 0$!

Even if T = 0 K!

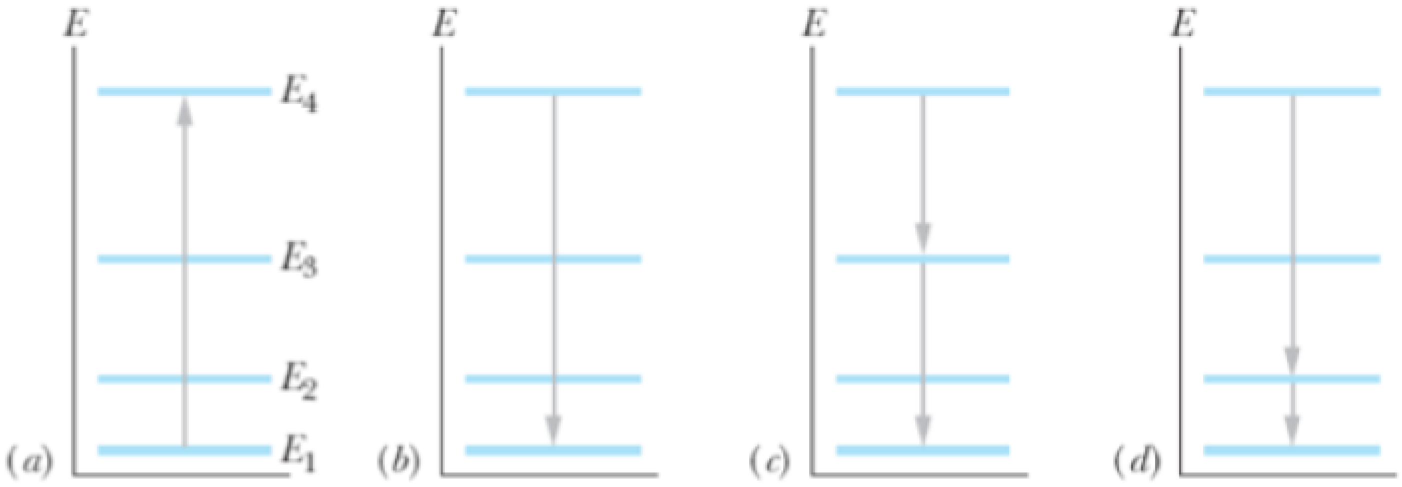
Therefore in quantum physics, *confined systems* cannot exist in states with zero energy. They must always have a certain minimum energy called the zero-point energy.

Absorption of photon by a trapped electron

If a confined electron is to absorb a photon to make a quantum jump (be excited to another level as in (a)), the **energy *hf* of the photon must equal the energy difference Δ*E* between the initial energy level of the electron and a higher level**:

$$\Delta E = hf = \frac{hc}{\lambda} = E_{high} - E_{low}$$

The electron does not stay in the excited state, instead it de-excites by releasing a photon. Some allowed transitions are shown below in (c) - (d).



Absorption/Radiation of photon by a trapped electron

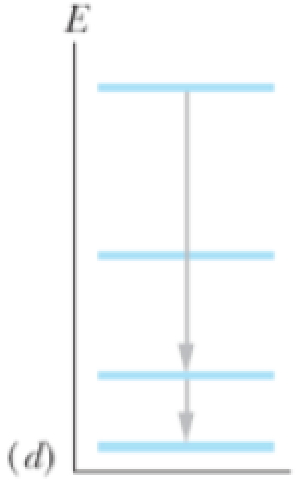
(Bit of background theory, to help you link quantum with classical picture)

- Find the expected (average) position of the electron using the wave function.

- This is a constant position if the electron is a single state, it doesn't oscillate.

(more quantum weirdness)

- But if the electron is simultaneously in two states e.g. $\Psi = a\Psi_1 + b\Psi_2$ and *a* and *b* evolve with time (e.g. start with *a*=1 and *b*=0) then **expected position oscillates and hence radiates as a cosine with frequency** $f = \frac{E_2 - E_1}{h}$



The electron "distribution" in two states leads to back and forth motion of the electron

Atomic Dipole Transitions Applet (falstad.com)

refresher https://youtu.be/FWCN_uI5ygY

Example 2

An electron is trapped in a one-dimensional infinite well of width 450 pm and is in its ground state. What are the

a. longest,

b. second longest, and

c. third longest wavelengths of light that can excite the electron from the ground state via a single photon absorption?

Example 2 cont.

An electron is trapped in a one-dimensional infinite well of width 450 pm and is in its ground state. What are the

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Wave functions of a trapped electron

The probability $p(x)$ that an electron can be detected at position x within the well is:

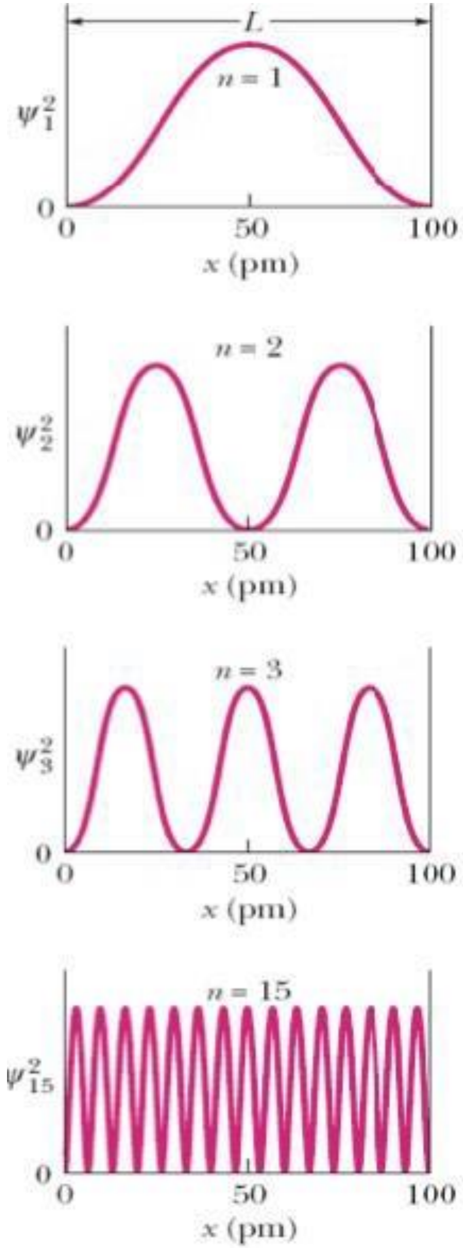
probability $p(x)$ of detection in width dx centred on position x = probability density $\psi_n^2(x)$ at position x . width dx

$$p(x) = \psi_n^2(x)dx$$

For an electron trapped in the one dimensional well

$$\psi_n^2(x) = A^2 \sin^2\left(\frac{n\pi}{L}x\right), \qquad \text{for} \quad n = 1, 2, 3, \ldots \ldots$$

for $0 \leq x \leq L$. Note the wave function is zero outside that range. The probability density for L = 100 pm is shown in the diagram for a number of levels.



Wave functions of a trapped electron – finding A

To find the probability of detecting the electron in a finite region (say between x_1 and x_2) we must integrate between those points

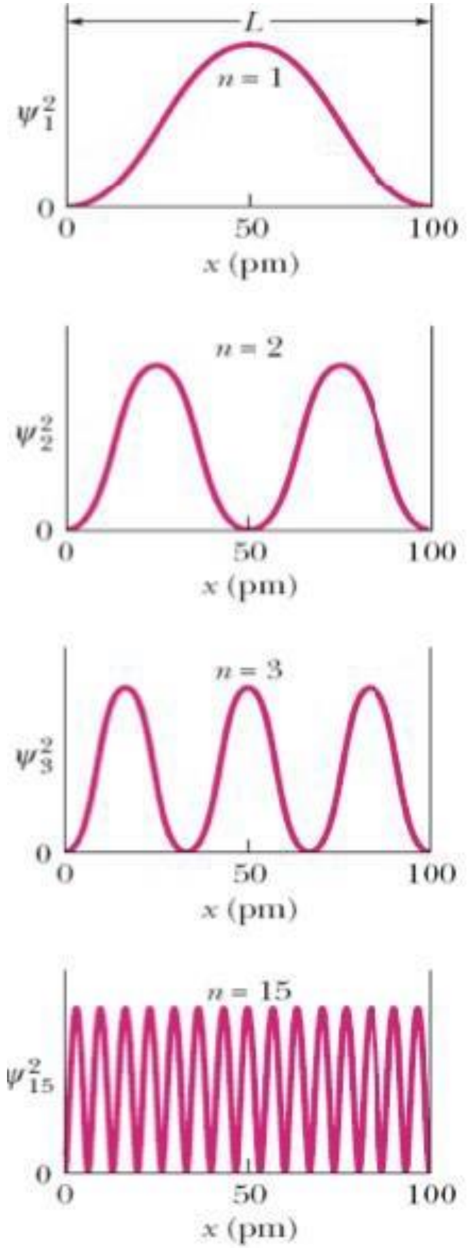
$$\text{Probability} = \int_{x_1}^{x_2} \psi_n^2(x)\,dx = \int_{x_1}^{x_2} A^2 \sin^2\left(\frac{n\pi}{L}x\right) dx$$

The probability of detecting the electron between $-\infty < x < \infty$ is ONE (normalisation condition) therefore for an infinite potential well of width *L.*

$$1 = \int_0^L A^2 \sin^2\left(\frac{n\pi}{L}x\right) dx$$

Evaluating gives

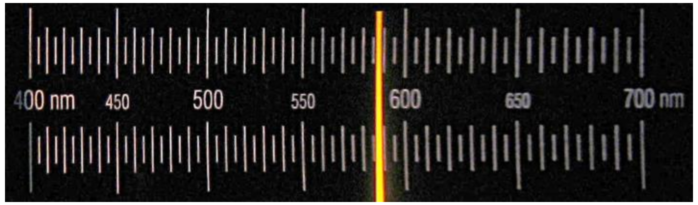
$$A^2 = \frac{2}{L}$$

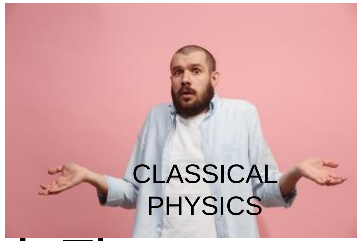


Sec. 39.2

Electron orbiting an atom - Neils Bohr’s model

- The problem: classical theory can show why an atom radiates (circular motion -> acceleration -> radiation) BUT it predicts a continuous spectrum, not the line spectra seen in experiments.



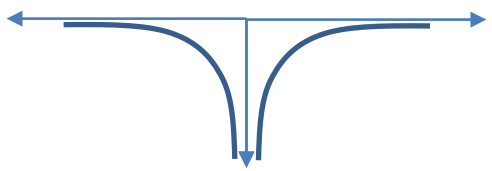


- In 1913, Danish physicist Niels Bohr (a student of both Thomson and Rutherford) further refined the nuclear model by proposing that:
  - electrons moved only in restricted, successive **orbital shells**
  - the outer, higher-energy orbits determined the chemical properties of the different elements.
- Bohr was able to explain the spectral lines of the different elements by suggesting that as electrons jumped from higher to lower orbits, they emitted energy in the form of a single photon.

Bohr model of the hydrogen atom

Coulomb's force attracts the electron to the proton:

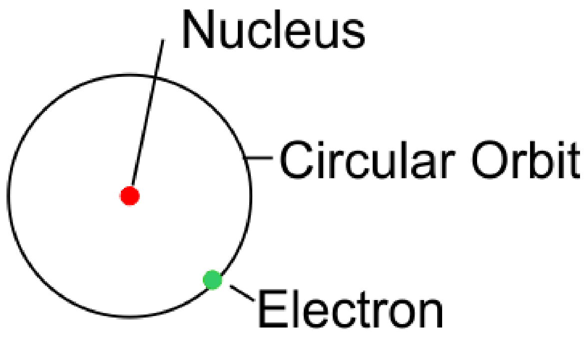
$$F = k\frac{|q_1 q_2|}{r^2} \quad \rightarrow U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$



Substitute this into the SE in spherical coordinates and a miracle occurs.

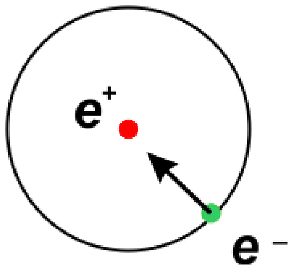
As for the electron in a well, the SE predicts allowed constructive interference states.

In this case, the wave function has to constructively interfere in with itself in a spherical path.



This is a 3D problem so we have 3 quantum numbers:

- *n* – the *principal* quantum number, can be any integer
- *l* – the angular momentum quantum number, < *n*
- m_l – the magnetic quantum number



Bohr theory:- orbital energy is quantised cont….

The energy levels corresponding to different states depend only on *n*:

$$E_n = -\frac{1}{8}\frac{me^4}{\varepsilon_0^2 h^2}\frac{1}{n^2} \qquad \text{for } n = 1, 2, 3, \ldots \ldots$$

Substituting in constants:

$$E_n = -\frac{2.18 \times 10^{-18}\ \mathrm{J}}{n^2} = -\frac{13.6\ eV}{n^2}$$

Which is the same result as Bohr's (but he didn't use the SE or know why energy should be quantised)

Using the SE instead of Bohr's ad hoc classical approach allows us to predict other properties such as:

- The nature of the electron motion in the orbits
- The probable location of the electron
- The nature of the transition between energy states

Bohr theory:- how energy changes in the hydrogen – association with wavelength

Atomic energy gain or loss is associated with one photon

$$hf = \Delta E = E_{high} - E_{low}$$

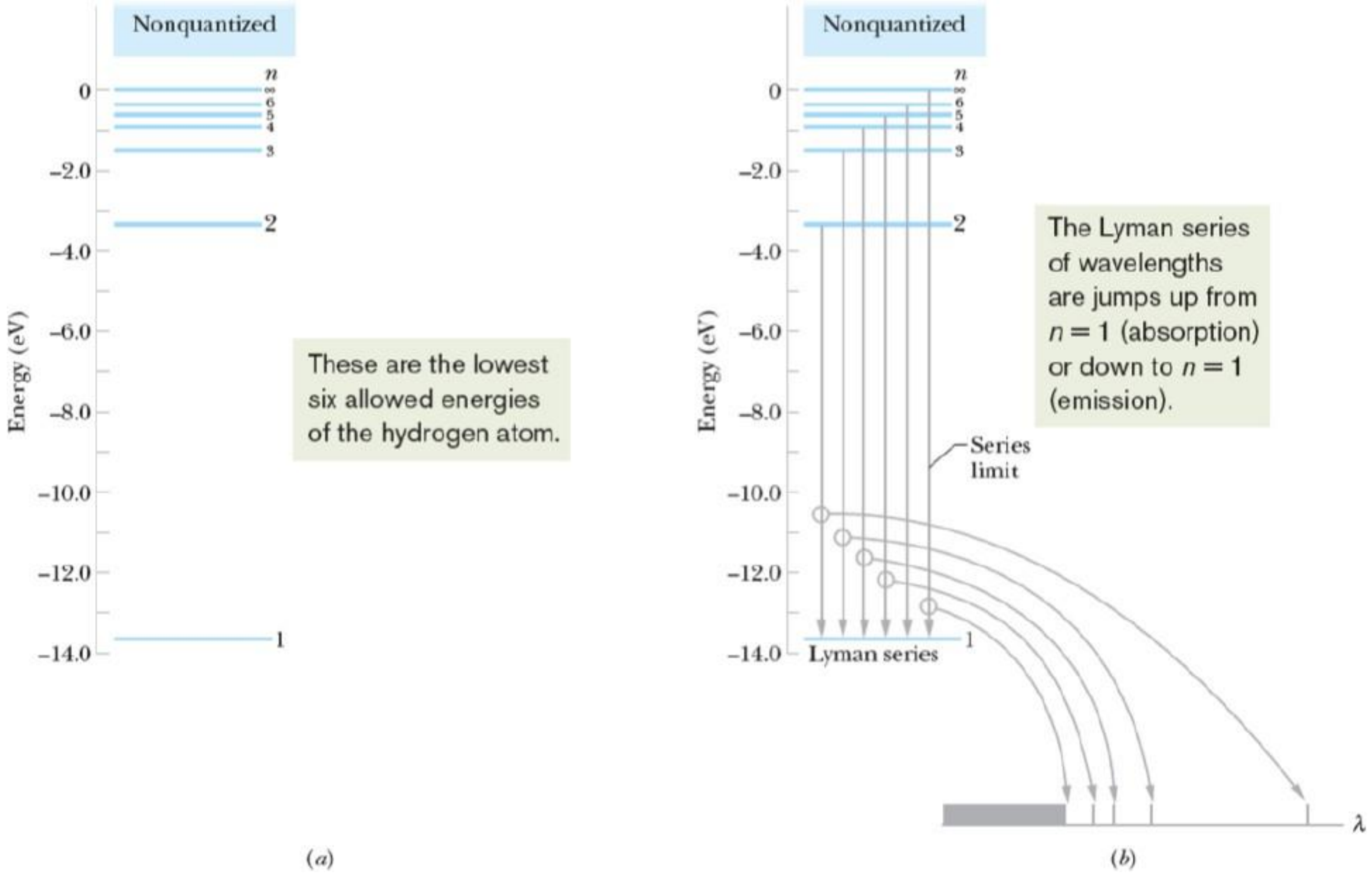
Also

$$hf = \frac{hc}{\lambda} = \Delta E_n = -\frac{1}{8}\frac{me^4}{\varepsilon_0^2 h^2}\frac{1}{n_{high}^2} - -\frac{1}{8}\frac{me^4}{\varepsilon_0^2 h^2}\frac{1}{n_{low}^2}$$

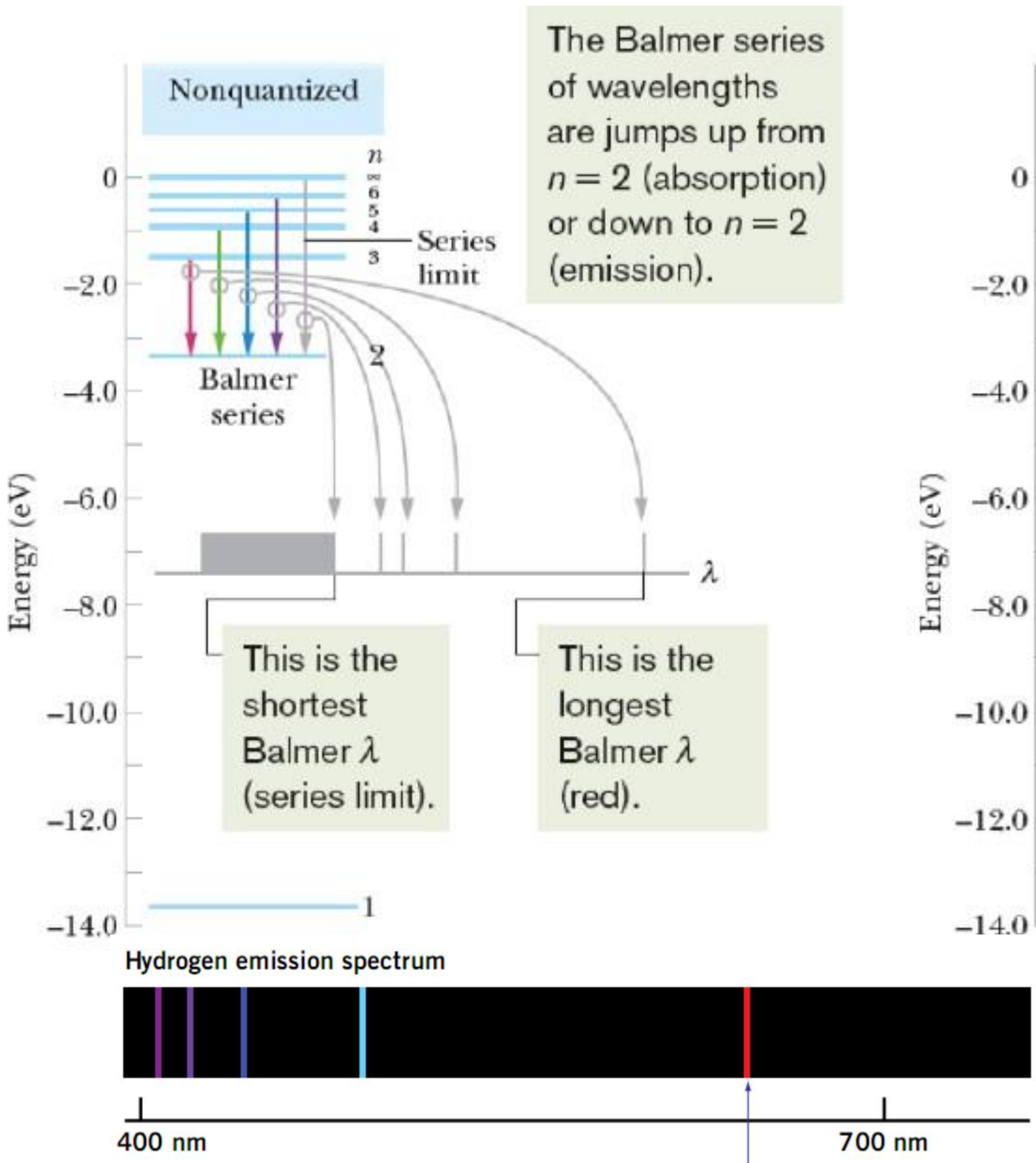
$$\frac{1}{\lambda} = \frac{1}{8}\frac{me^4}{\varepsilon_0^2 h^3 c}\left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2}\right) = R\left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2}\right)$$

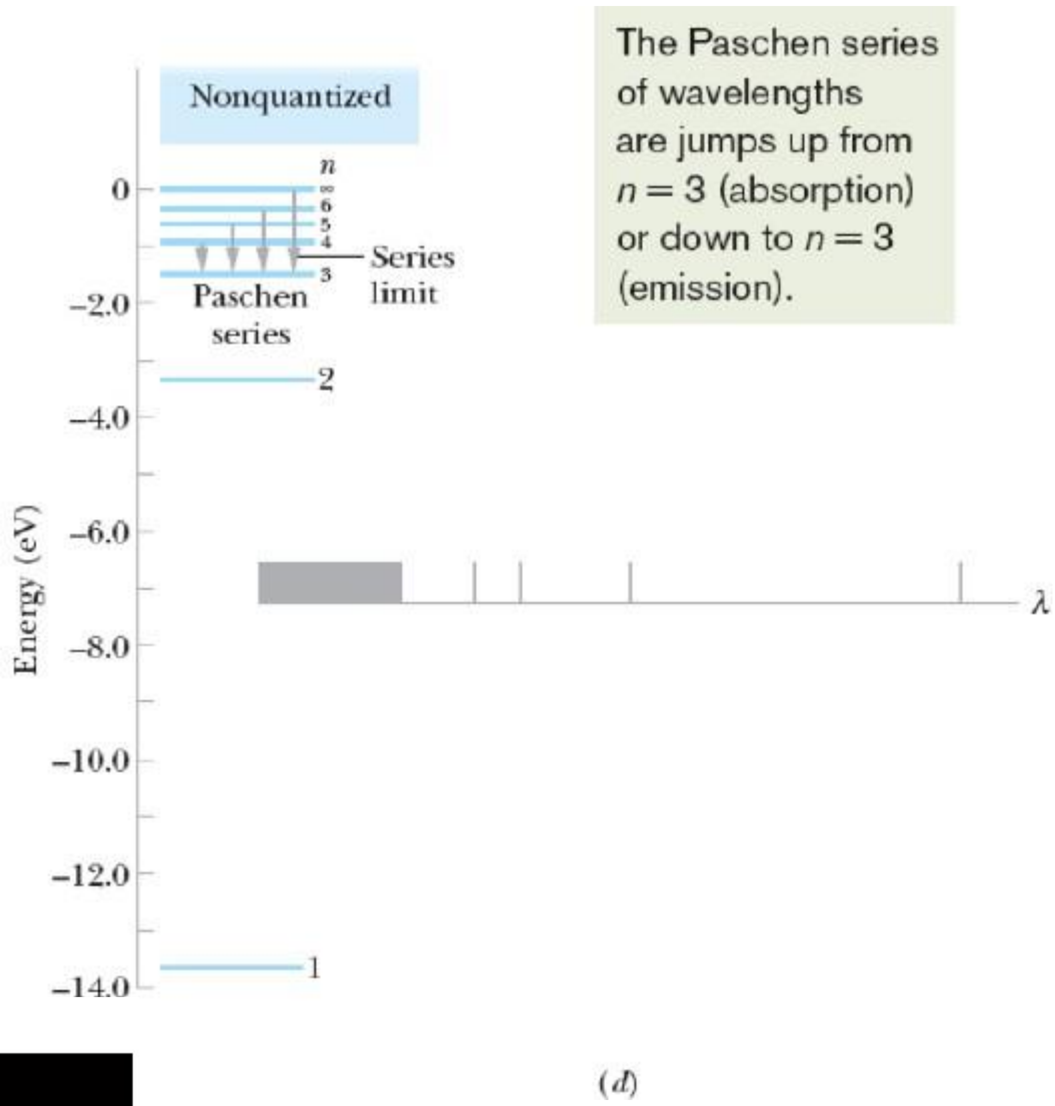
$R = \frac{1}{8}\frac{me^4}{\varepsilon_0^2 h^3 c} = 1.097373 \times 10^7 \mathrm{m}^{-1}$ is known as Rydberg's constant.

Energy Level diagram for hydrogen atom (I)



Energy Level diagram for hydrogen atom (II)





Example 1

What are the emitted photon’s

a. energy,

b. magnitude of the momentum, and

c. wavelength

when a hydrogen atom undergoes a transition from a state with n = 4 to a state with n = 2 (from Balmer series)?