Lecture 1. The dawn of the quantum theory

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Why do we need quantum mechanics?

In classical mechanics, knowing the initial condition of the object (such as initial configuration and velocity) determines the trajectory via *Netwon's 2nd law*, or equivalently, *Hamilton's equation of motion*.

$$\mathbf{F} = m\mathbf{a} \qquad \frac{\partial H}{\partial p_i} = \dot{q}_i, \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i$$

In atomic scale, classical things you know does not work anymore. In microscopic world, objects follow new equation of motion called *Schrödinger's equation*. More on this later.

In this lecture, we discuss the dawn of the quantum theory.

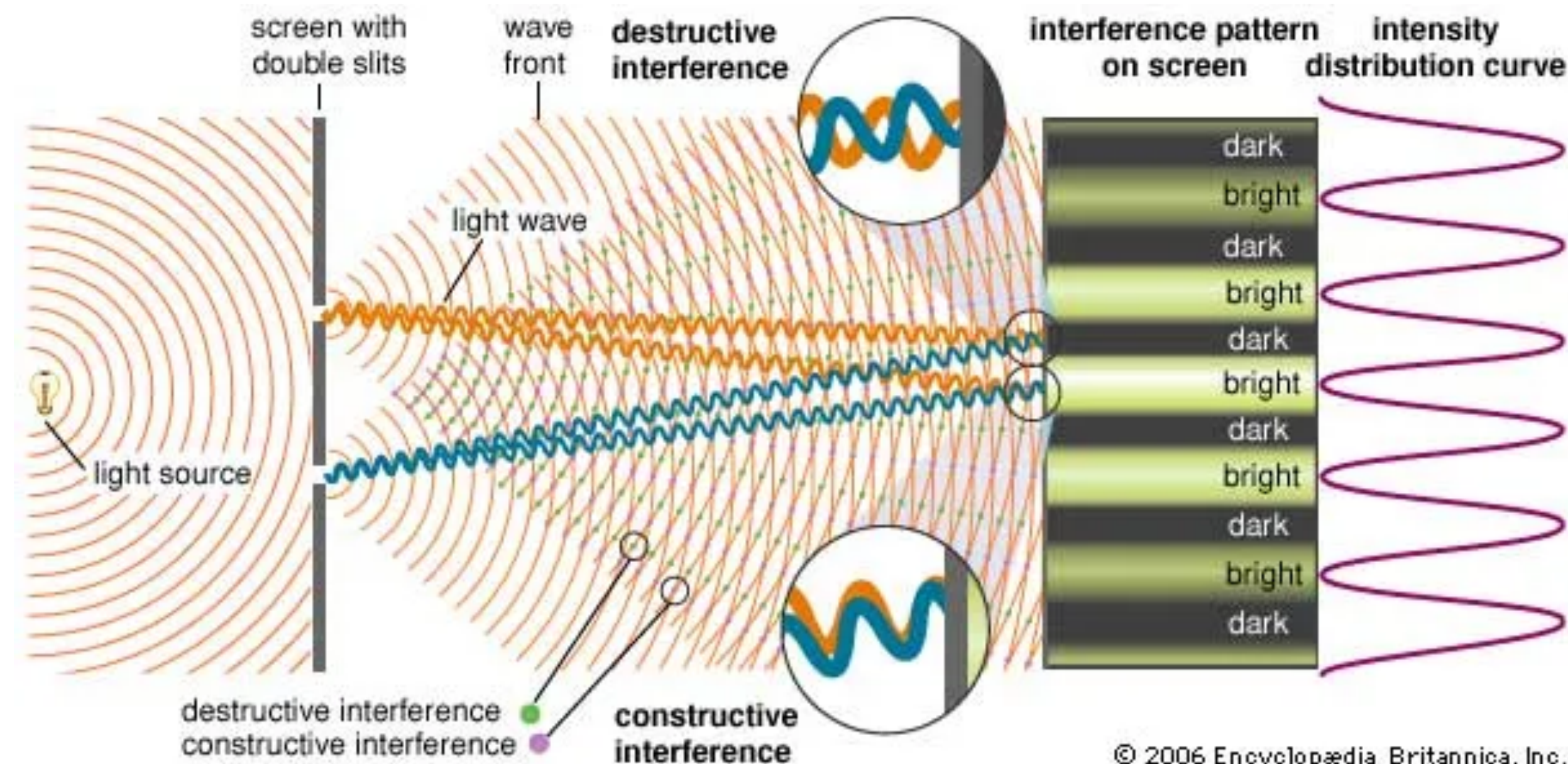Let's go back to the late 19th ~ early 20th century.

Preliminary: Let there be light.

Classically, light is **wave** that travels in speed of light, c.

$$c = \lambda\nu$$

The speed of light is a product of wavelength and frequency.

Light is indeed wave since it exhibits the *interference* phenomenon.

From Encyclopedia Britannica

Color and temperature

STAR COLOR TEMPERATURE CHART

COLOR	EXAMPLE	SURFACE TEMP IN CELSIUS
	SPICA	28,000 - 11,000
	VEGA	11,000 - 7,500
	THE SUN	6,000 - 5,000
	ARCTURUS	5,000 - 3,600
	ANTARES	3,600 - 2,000

astrobackyard.com

The hotter a star, the shorter the wavelength.

This phenomenon is not limited to the stars. When someone tries to melt the iron ingot, it is black before heating. However, as temperature rises, iron gets red and yellow.

A **blackbody** is an ideal matter that is capable of absorption and emission of all light (regardless of its wavelength).

When a blackbody is heated, it emits radiation (a **blackbody radiation**). Then, at given temperature, what is the distribution of wavelengths radiated by the blackbody?

Blackbody radiation

With classical mechanics, *Rayleigh-Jeans law* can be derived. However, it could not describe the experimental intensity curve somehow. Note that the intensity of light is proportional to the square of frequency. This is called an **ultraviolet catastrophe**.

$$\rho_\nu(T)d\nu = \frac{8\pi\nu^2}{c^2}kT\,d\nu$$

Investigating the shape of experimental curve, Max Planck managed to find the mathematical expression of blackbody radiation curve. This is called the *Planck's law* or *Planck distribution*. This distribution contains one new constant value, the **Planck constant**. We are now in year 1900.

$$\rho_\nu(T)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3\,d\nu}{e^{h\nu/kT}-1}$$

Blackbody radiation

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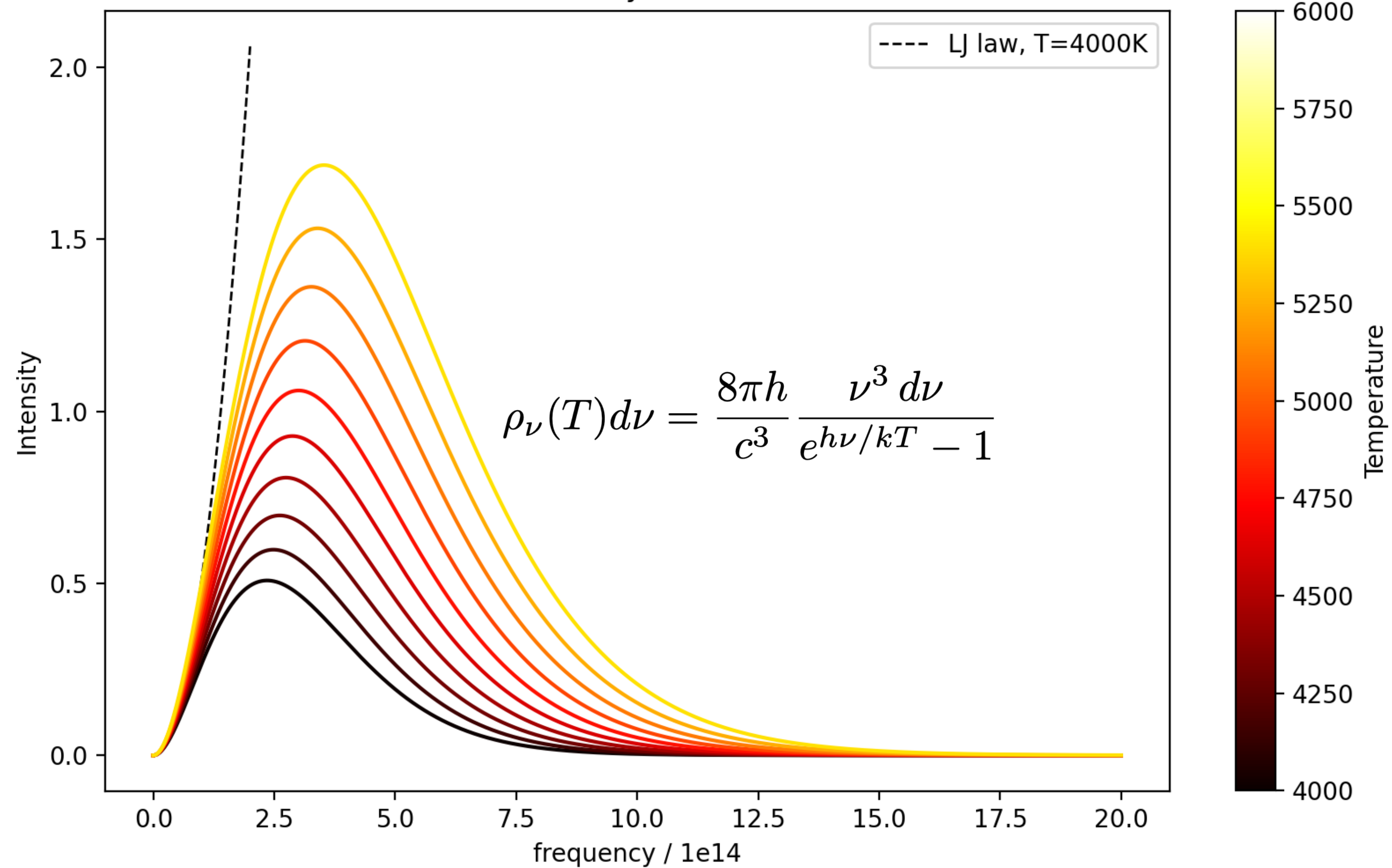
Blackbody radiation

What is the physical meaning of Planck distribution?
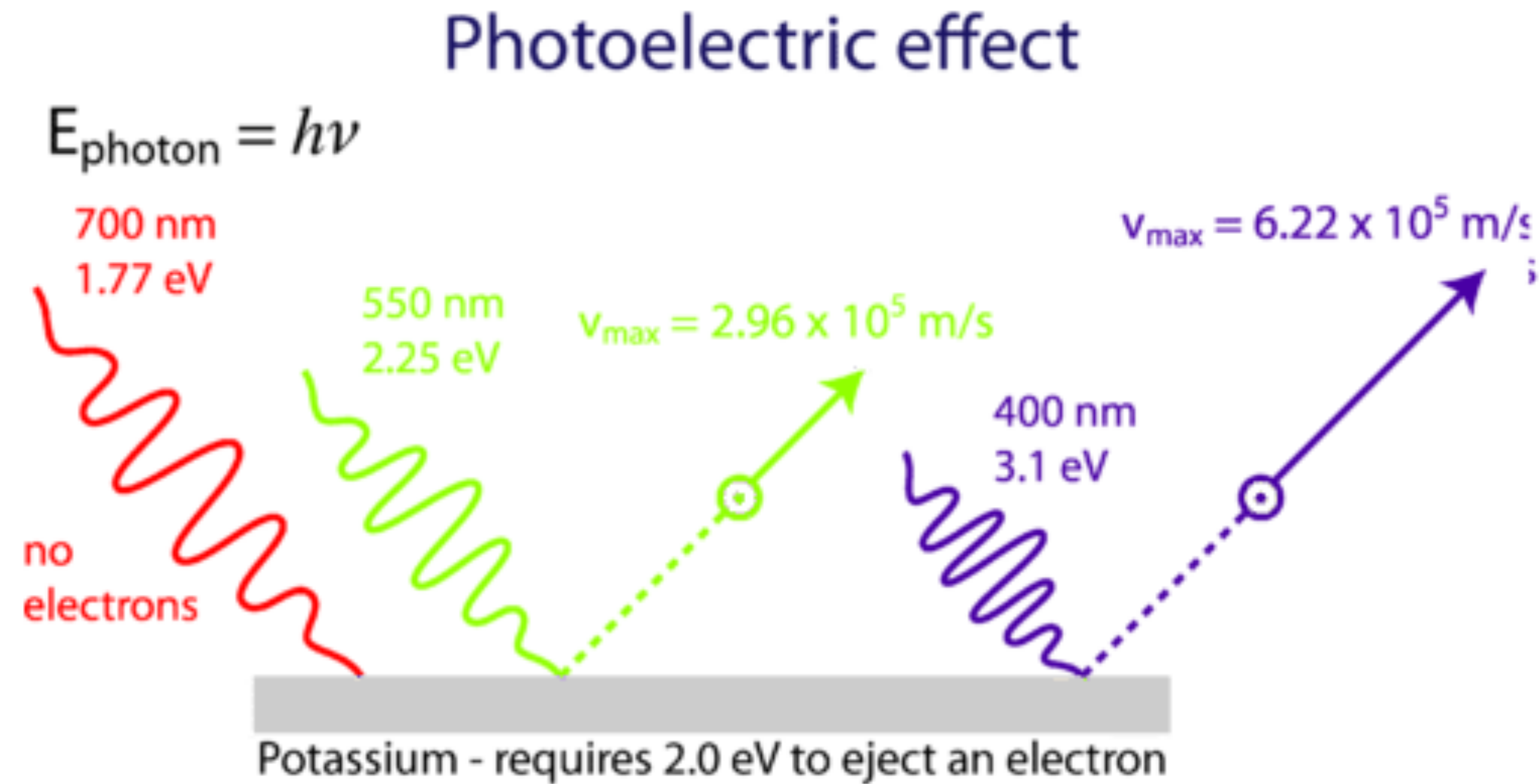
Assume that atoms in blackbody oscillate when they are heated, and these oscillators can have **quantized** energy, E, 2E, 3E, and so on. From this quantization hypothesis, Planck distribution can be derived.

But why? No one can answer this question, and everyone considered this conclusion as a bizarre one.

However, there were two more unsolved problems, which gave awkward conclusions.

Photoelectric effect

When light is irradiated on the metallic surface, photoelectron is emitted. This phenomenon is called a **photoelectric effect.**

Photoelectric effect

$E_{photon} = h\nu$

700 nm
1.77 eV

550 nm
2.25 eV

$v_{max} = 2.96 \times 10^5$ m/s

$v_{max} = 6.22 \times 10^5$ m/s

400 nm
3.1 eV

no
electrons

Potassium - requires 2.0 eV to eject an electron

Photoelectric effect

Physicists measured the kinetic energy of photoelectron. However, the experimental results were awkward.

1. Under certain frequency, no photoelectrons are emitted regardless of the intensity of light. However, if frequency exceed that certain frequency (we call this a *threshold frequency*), even if the intensity is really weak, photoelectrons are emitted.

2. Over the threshold frequency, number of photoelectrons is proportional to the intensity of light.

Remember that physicists at that time considered light as a wave.

Photoelectric effect

However, if one considers light as a **particle**… then experimental results can be explained.

Albert Einstein did this in 1905.

Digression: Year 1905 is often called *Annus Mirabilis*. In 1905, Einstein published history-changing papers.

One of them is his paper about photoelectric effect, which gave him a Nobel Prize.

Second one is about the Brownian motion, which is a strong evidence of the existence of atoms. More on this later.

Last one (actually, two papers) is about the *special theory of relativity*.

Photoelectric effect

Einstein postulated the *quantization of light energy*. Nowadays we call this *photon*. A photon has energy proportional to its frequency, with some constant *h*.

$$E = h\nu = h\frac{c}{\lambda}$$

To remove an electron from the metallic surface, energy is required (similar with *ionization energy*). We call this a *work function*. Remaining energy after the ionization is stored in the kinetic energy of photoelectron, which we can measure.

$$E = h\nu = \phi_0 + \frac{1}{2}mv^2$$

Theoretically, at the threshold frequency, photoelectron is emitted with zero kinetic energy. Therefore,

$$\phi_0 = h\nu_0$$

Photoelectric effect

One can plot the kinetic energy of photoelectron with respect to the frequency of light. Surprisingly, the proportionality constant in the energy quantization hypothesis was same with the constant introduced in the Planck distribution.

This was not a coincidence.

Digression. Einstein's quantization hypothesis opened the era of quantum mechanics. However, Einstein himself did not trusted quantum mechanics until he passed away. He could not embrace the "randomness" inside the quantum mechanics. Einstein debated about this issue with Bohr, Heisenberg, and other famous physicists who created the theoretical framework of quantum mechanics.

The wave-particle duality

Recall that the light is a wave, classically.

However, photoelectric effect cannot be explained by considering light as wave.

Interference cannot be explained by considering light as particle.

Scientists have concluded that light exhibits **wave-particle duality**.

Digression: What is wave and particle

Consider a plane wave, which is clearly "wave":

$$\psi(x) = e^{i(kx - \omega t)}$$

Ignore time for simplicity. Fourier transform with respect to *x*:

$$\mathcal{F}[\psi(x)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} e^{-ipx} \, dx = \frac{\delta(k - p)}{2\pi}$$
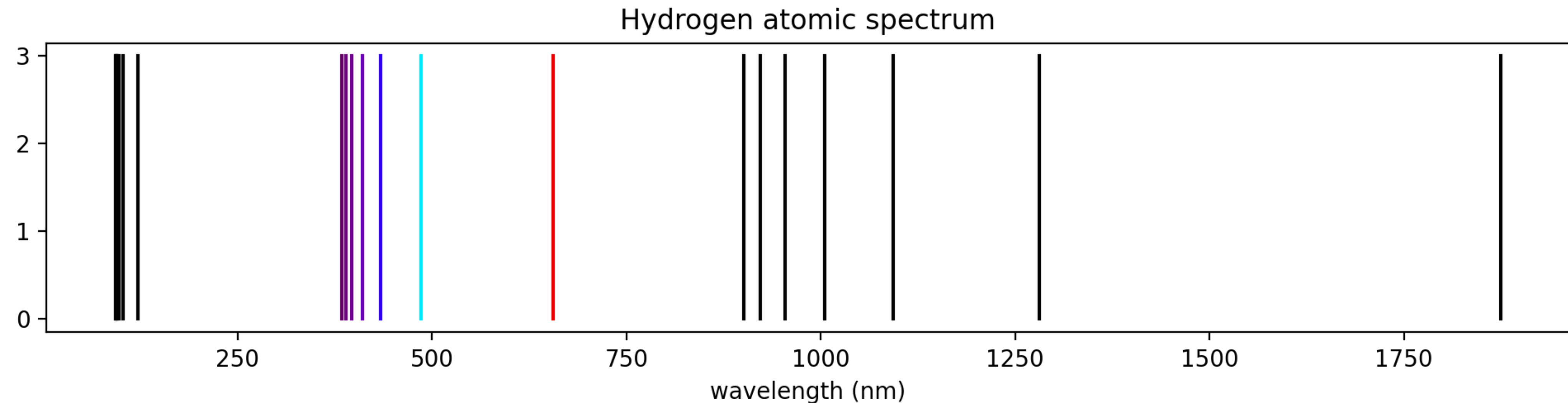
This states that wave is delta-function in *p*-space. Meanwhile, consider a localized "pulse".

$$\psi(x) = \delta(x - x_0)$$

Clearly, representation in *p*-space should be plane-wave-like. More on this later.

Oh, line spectrum, talk to me!

Another unsolved problem was a **line spectrum of atom**.

The empirical relation between spectrum lines is discovered by Johann Balmer, in 1885.

Oh, line spectrum, talk to me!

This is the **Balmer formula**.

$$\frac{1}{\lambda} = 109680 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \text{ cm}^{-1}$$

However, no one can explain this result. Recall the level of "atomic models" in late 19th century.

Bohr Model

In 1911, Niels Bohr presented a theory of hydrogen spectrum. He assumed that electrons move along certain circular orbits around the nucleus. The classical equation of motion is: electromagnetic attraction is the source of centrifugal force.

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}$$

In addition, Bohr suggested two more postulates. First one was **angular momentum quantization**.

$$L = mvr = n\hbar = n\frac{h}{2\pi} \ (n = 1, 2, 3, \dots)$$

Second one was **frequency condition**. Electron can make transition between two orbits, and absorbs (or emits) the difference of energy of orbits as photon.

$$\Delta E = E_n - E_m = h\nu$$

Bohr Model

From the angular momentum quantization, $v = \dfrac{n\hbar}{m_e r}$

Substitue this to yield $r = \dfrac{4\pi\epsilon_0 \hbar^2}{m_e e^2} n^2 = a_0 n^2$ where a_0 is called **Bohr radius** (~0.53 Angstroms).

Total mechanical energy of this system is a sum of kinetic and (electromagnetic) potential energy.

$$E = T + V = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -\frac{1312}{n^2} \, (\mathrm{kJ/mol}) = -\frac{13.6}{n^2} \, (\mathrm{eV})$$

Using the frequency condition, we can reproduce the Balmer's formula.

$$\Delta E = \frac{hc}{\lambda} = 1312 \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \, (\mathrm{kJ/mol})$$

Therefore, Bohr model could explain the hydrogen line spectrum problem!

Bohr Model is wrong.

Q1. Why should angular momentum be quantized?

A1. de Broglie's **matter wave** concept can explain this. Momentum of photon is given by

$$p = \frac{h}{\lambda} \implies \lambda = \frac{h}{p}$$

Therefore, for the particle (like electrons, small nuclei, etc.), one can define "wavelength".

$$\lambda = \frac{h}{mv}$$

Bohr Model is wrong.

If one assume that electron's matter wave should form standing wave along the orbit, angular momentum quantization condition can be derived.

$$2\pi r = n\lambda \; \rightarrow \; 2\pi r = n\frac{h}{mv}, \; mvr = n\frac{h}{2\pi}$$
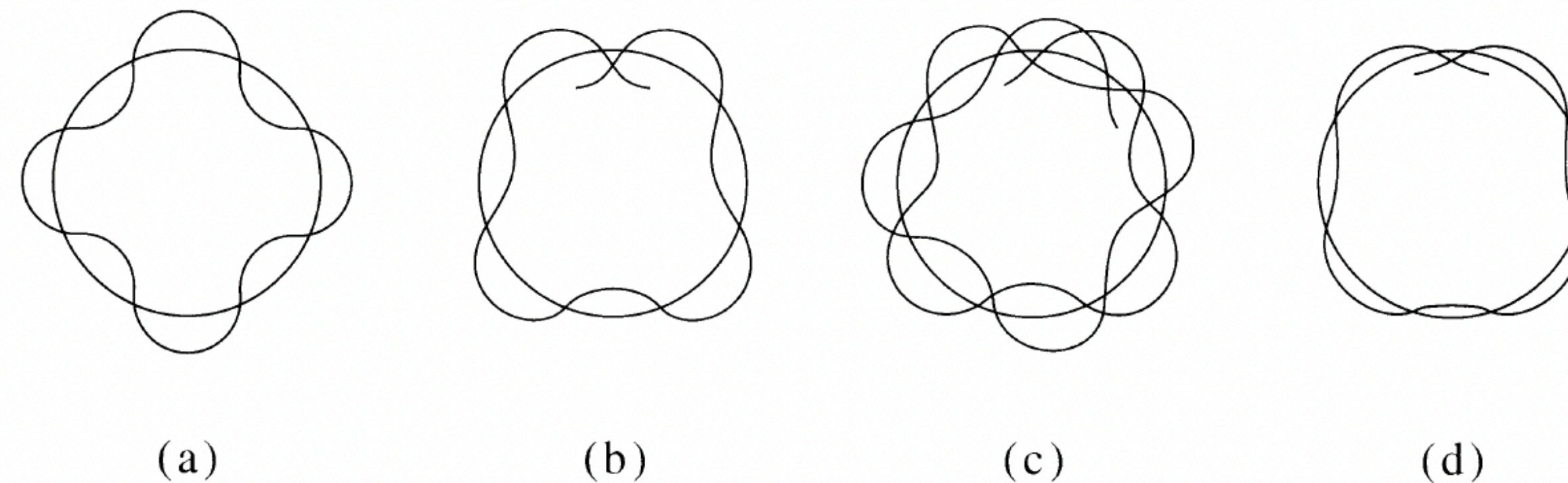

(a)　　　　　(b)　　　　　(c)　　　　　(d)

FIGURE 1.9
An illustration of matching and mismatching de Broglie waves travelling in Bohr orbits. If the wavelengths of the de Broglie waves are such that an integral number of them fit around the circle, then they match after a complete revolution (a). If a wave does not match after a complete revolution (b), cancellation will result and the wave will progressively disappear (c, d).

Bohr Model is wrong.

Q2. What if there were more than one electron?

Q3. Electrons are accelerated in the circular motion. Then electron, a charged particle, should radiate electromagnetic radiation and lose its energy, and the orbit would collapse toward the nucleus. How can it be possible?

Bohr model could not answer this question.

Moreover, the concept that we can exactly know the position and momentum of the electron was fundamentally wrong. We can't do it in quantum mechanics.

Heisenberg's uncertainty principle

In quantum mechanics, *"measurement"* takes up such an important role. Let's take an simple example about measurement. Suppose that you are monitoring the trajectory of tennis ball.

γ

$\mathbf{v}(t)$

$(x(t), y(t), z(t))$

γ
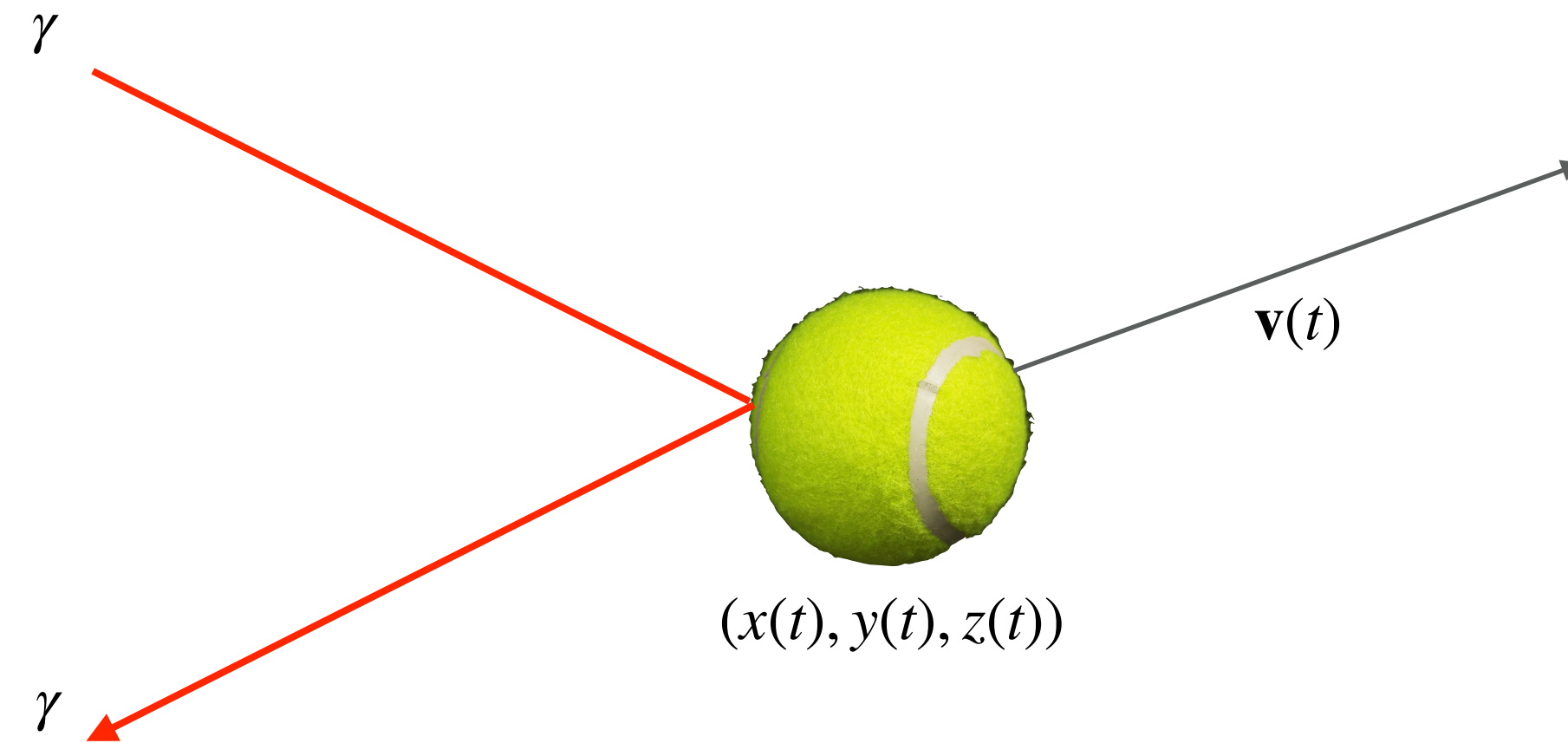
To *"measure"* the location of the tennis ball, a photon must interact with the electron. However, since tennis ball is macroscopic object, its momentum is not changed so much. However, consider the *measurement of the position of an electron.*

Heisenberg's uncertainty principle

However, consider the *measurement of the position of an electron.*
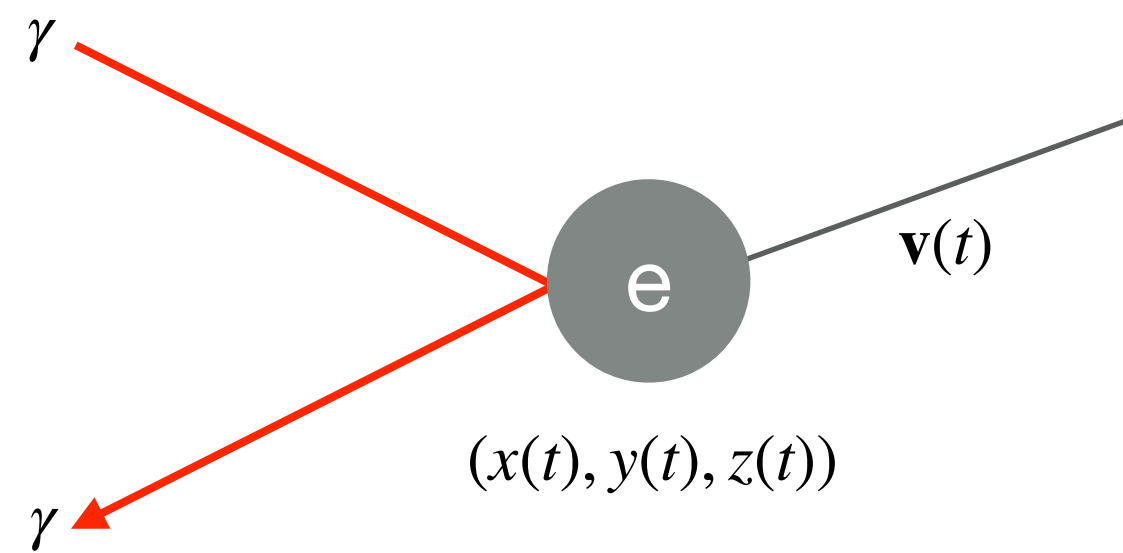
If we wish to locate the electron within the distance Δx, we need to use light with a wavelength of $\lambda \sim \Delta x$. Since photon has a momentum $p = h/\lambda$, some of this momentum will be transferred to the electron. **The very act of locating the electron leads to a change in its momentum.**

Moreover, if we wish to locate the electron more accurately, we must use a light with a smaller wavelength, which gives larger uncertainty for the momentum measurement.

To decrease the uncertainty of momentum, we need to use light with longer λ, which has low resolution(i.e., large Δx).

Heisenberg's uncertainty principle

A careful analysis of this process was carried out in the mid-1920s, by the German physicist **Werner Heisenberg**(1901-1976).

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

The uncertainty principle states that, product of *standard deviations* of position and momentum measurements, is always larger than certain constant.

This is an uncertain, random nature of quantum mechanics. More on this later.

References of this lecture

If you are interested in "old quantum theory":

Tomonaga, S. *Quantum Mechanics, Vol. I: Old Quantum Theory*, 1st ed.; North-Holland Co., 1962.

If you are interested in "easier version":

Transnational college of LEX, 수학으로 배우는 양자역학의 법칙, *3판*.; 지브레인, 2020.

If you are interested in some exercises about the topics we dealt today:

McQuarrie, D. A.; Simon, J. D. The Dawn of the Quantum Theory. In *Physical Chemistry: A Molecular Approach,* 2nd ed.; University Science Books, 1997; pp 1-30.

If you are interested in derivation of RJ law and Planck law,

https://edisciplinas.usp.br/pluginfile.php/48089/course/section/16461/qsp_chapter10-plank.pdf

Atkins' Physical Chemistry textbook is always your companion, even though I do not mention it.