Physical Chemistry 2

Lecture 1. The Dawn of the Quantum Theory

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PChem 2

Physical Chemistry 2

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Topics in Lecture 1

Blackbody radiation and Planck distribution

Photoelectric effect and photon

Hydrogen atomic spectrum and Bohr model

de Broglie and matter waves

Uncertainty principle and nature of measurements

In Atkins' *Physical Chemistry* (11th ed.),

7A The origins of quantum mechanics
7C Operators and observables

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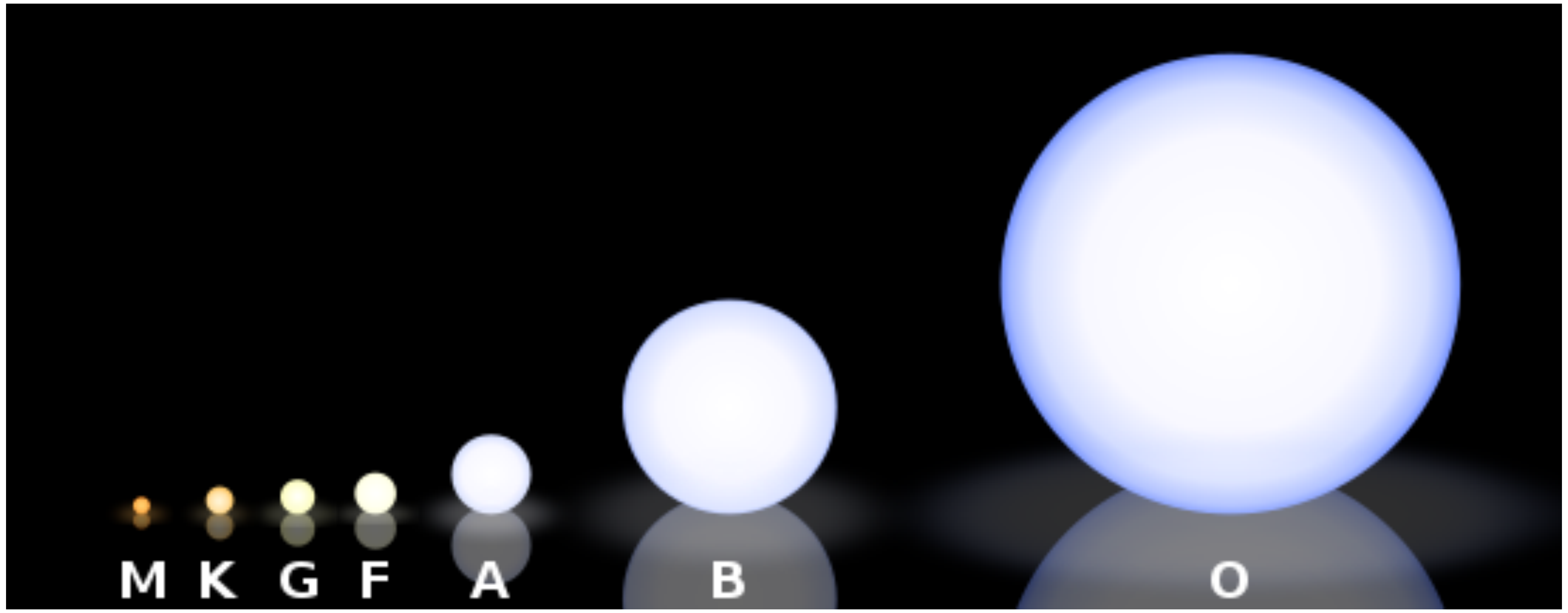
Blackbody Radiation

All objects emit *electromagnetic radiation* which range depends on the temperature of the object.
For instance, the hotter a star is, the more blue it shines.



Blackbody is a fictitious object that emits and absorbs any wavelengths of electromagnetic radiation.

Typically, blue objects absorb all but blue light; they reflect blue light. However, blackbody does not reflect any light (the name *black*body came from here).

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Blackbody Radiation

Question: At temperature *T*, what is the intensity of light for certain wavelength?

Of course, physicists tried to explain this phenomenon, with *Rayleigh-Jeans Law.*

$$\rho_\nu(T)\,d\nu = \frac{8\pi k_\mathrm{B} T}{c^3}\nu^2\,d\nu$$

$\rho_\nu(T)\,d\nu$ means the intensity of light, between ν and $\nu + d\nu$.

However, result of Rayleigh-Jeans Law was unphysical: intensity diverges as $\nu \to \infty$.

This problem is called *ultraviolet catastrophe.*

(Derivation of Rayleigh-Jeans law: in the Problem Set!)

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Blackbody Radiation

Max Planck assumed that the radiation emitted by the blackbody was caused by the *oscillations* of the electrons in the constituent particles of the material body.

Assumption: The energies of the oscillators are *discrete*, and had to be proportional to an *integral multiple of the frequency*

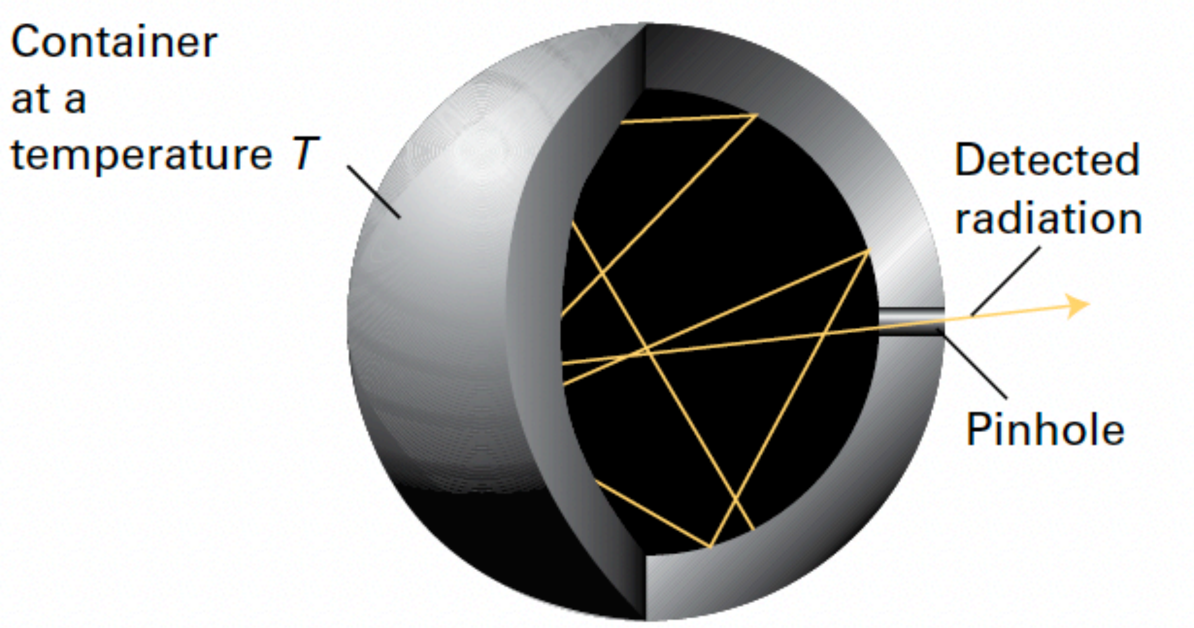

Figure 7A.1 Black-body radiation can be detected by allowing it to leave an otherwise closed container through a pinhole. The radiation is reflected many times within the container and comes to thermal equilibrium with the wall. Radiation leaking out through the pinhole is characteristic of the radiation inside the container.

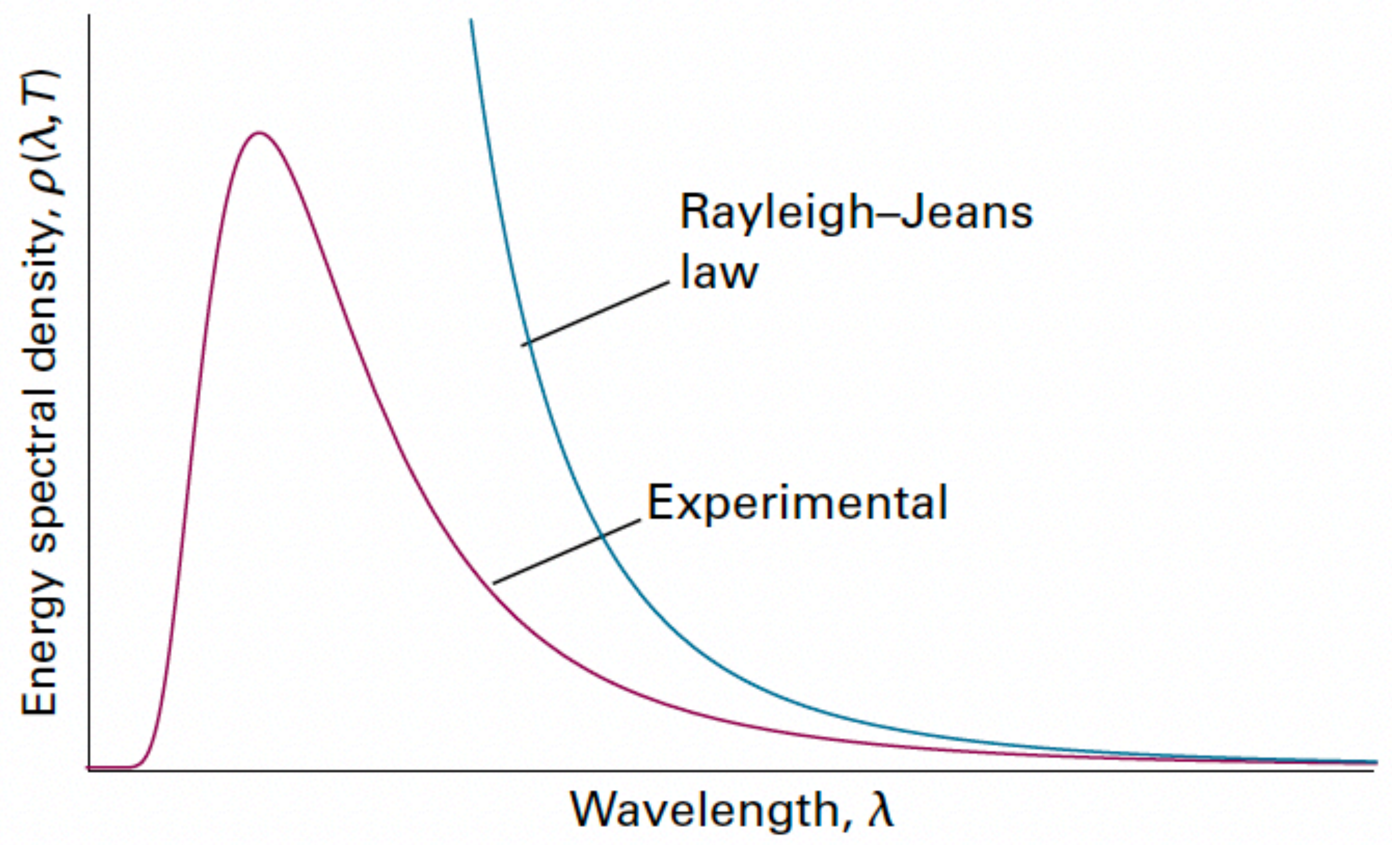

Figure 7A.3 Comparison of the experimental energy spectral density with the prediction of the Rayleigh–Jeans law (eqn 7A.4). The latter predicts an infinite energy spectral density at short wavelengths and infinite overall energy density.

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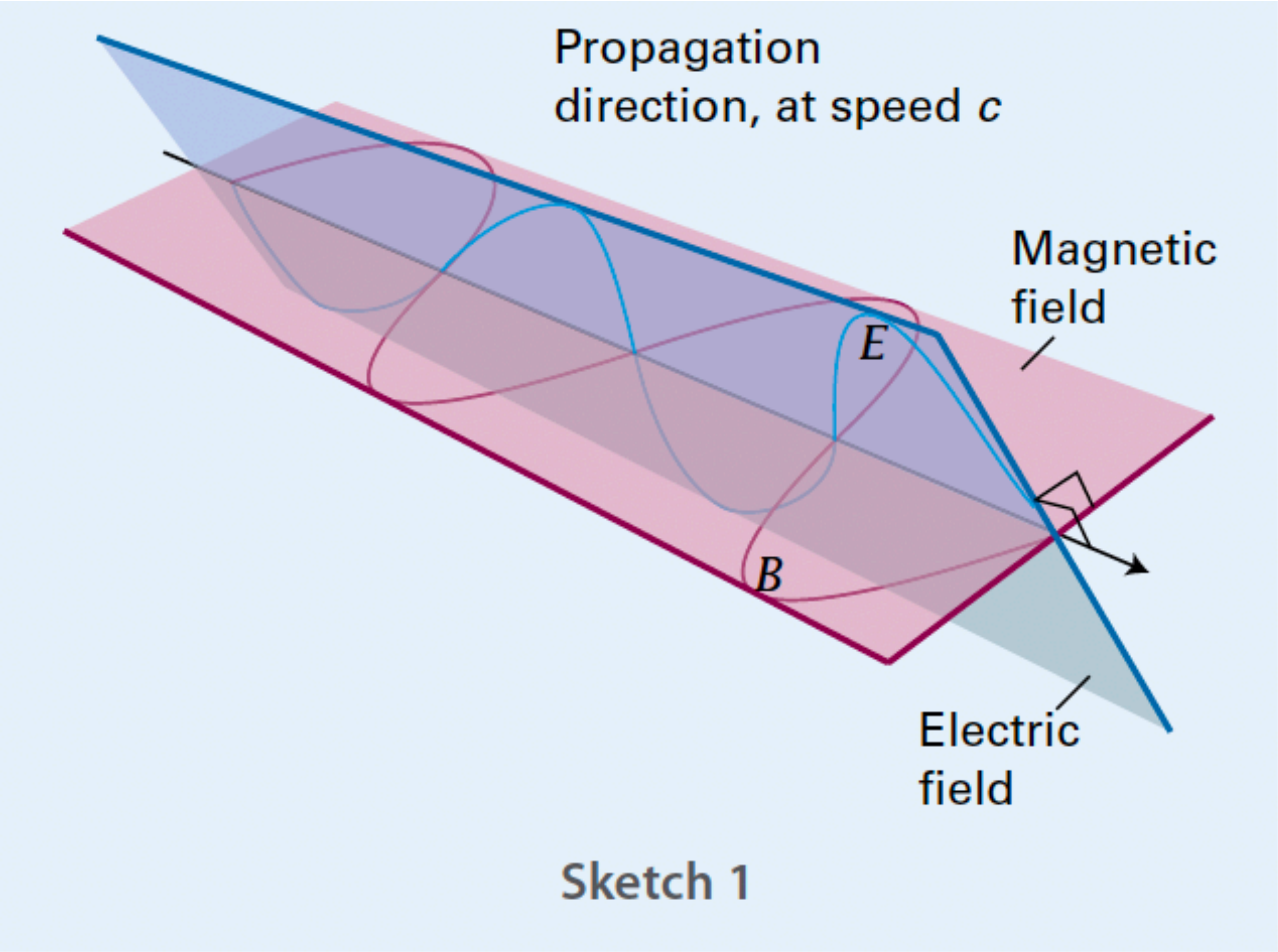
Light?

If you need to deal with quantum mechanics, you **should** be familiar with *wavelength, frequency, wavenumber, speed of light,* etc.

You have already learned that light is an electromagnetic wave that propagates without medium.



Speed of light, c, is given by

$$c = \lambda \nu$$

Where λ is a wavelength and ν is a frequency of light.

Wavenumber, $\tilde{\nu}$, is defined by

$$\tilde{\nu} = \frac{1}{\lambda}$$

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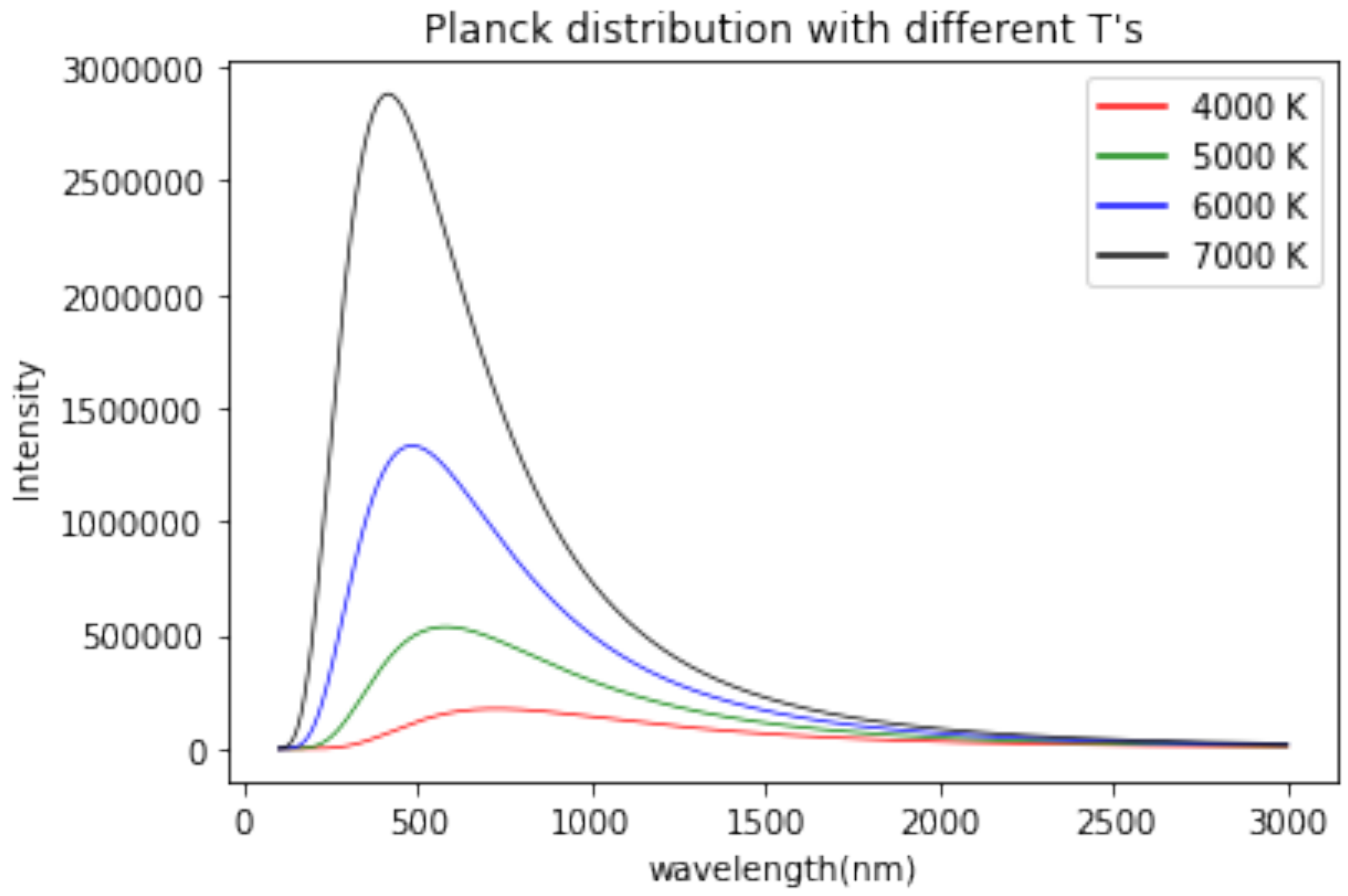
Blackbody Radiation

The *Planck distribution* is

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



We can use λ for Planck distribution, too.

$$c = \lambda\nu \implies d\nu = -c\frac{d\lambda}{\lambda^2}$$

$$\rho_\lambda(T)d\lambda = \frac{8\pi hc}{\lambda^5}\frac{d\lambda}{e^{hc/\lambda k_BT}-1}$$

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Blackbody Radiation

There are few consequences of Planck distribution.

1. **Stefan-Boltzmann law:** By integrating with respect to the Planck distribution, we can calculate total radiated energy from the blackbody.

$$E = \sigma T^4$$

2. Wien Displacement law: At each temperature *T*, there is a wavelength λ_{max} at which the intensity of the radiation is a maximum.

$$\lambda_{\text{max}} T = 2.9 \times 10^{-4}\,\text{m} \cdot \text{K}$$

3. Long wavelength limit: In $\lambda \to \infty$ limit, Planck distribution coincides with Rayleigh-Jeans law.

$$\lambda \to \infty \quad \Longrightarrow \quad \frac{h\nu}{k_{\text{B}}T} \to 0 \quad \Longrightarrow \quad \exp\left(\frac{h\nu}{k_{\text{B}}T}\right) - 1 \to \frac{h\nu}{k_{\text{B}}T}$$

(Detailed derivation: in the Problem Set!)

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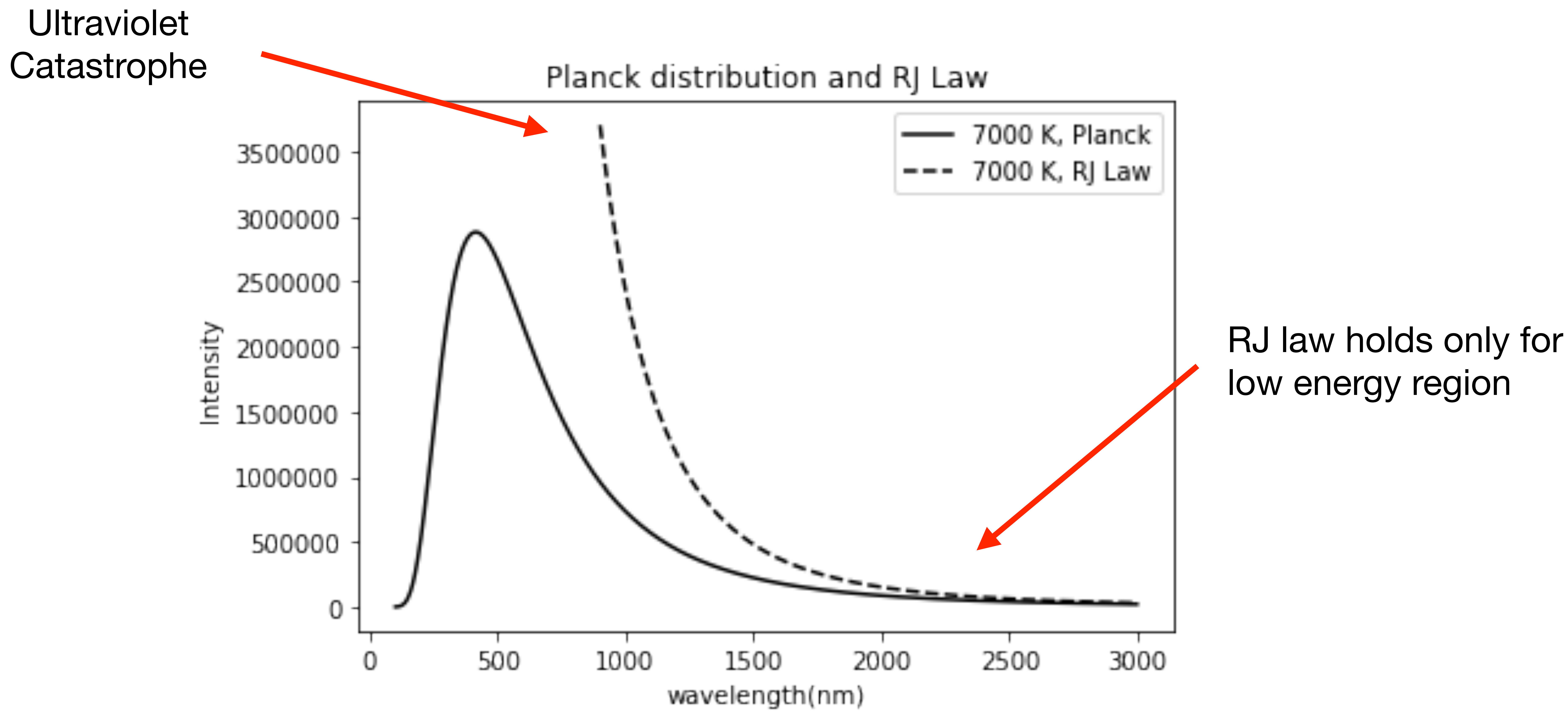
Blackbody Radiation



The Planck distribution is derived from the simple assumption: $E = nh\nu\ (n = 0,1,2,\ldots)$, which has completely changed the view of physics.

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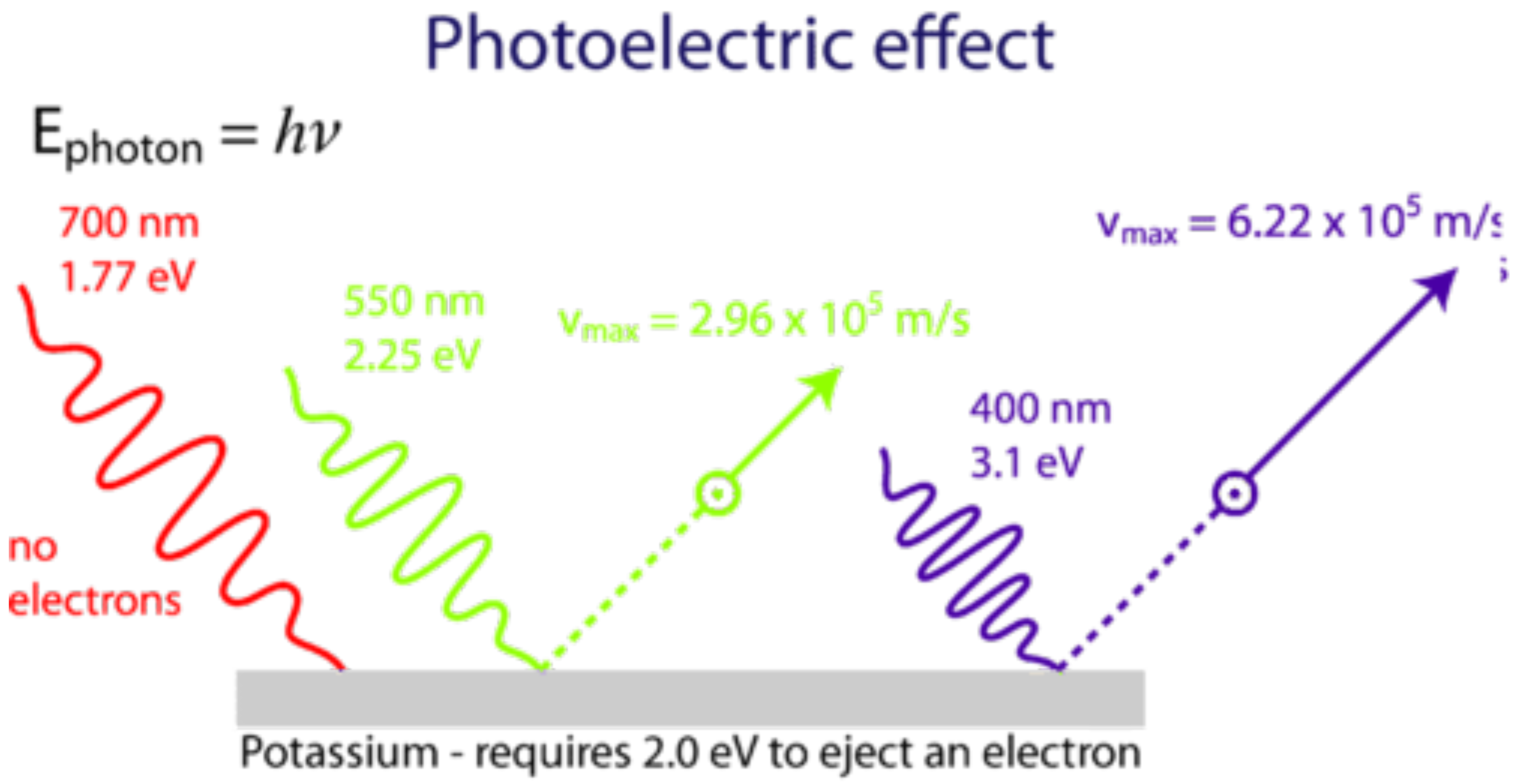
Photoelectric Effect

In 1886, Heinrich Hertz discovered that ultraviolet light (UV) causes electrons to be emitted from a metallic surface. But, something was wrong with the experiment result.

Kinetic energy of the ejected electron was intensity-independent.

Under the **threshold** frequency, no photoelectrons were observed.

However, beyond the threshold, photoelectrons were ejected proportional to the intensity of UV.



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Photoelectric Effect

To solve this mystery, Einstein used *Planck's quantum hypothesis*: Energy of the light exists in small packets of energy with $E = h\nu$, which is now known as a *photon*.

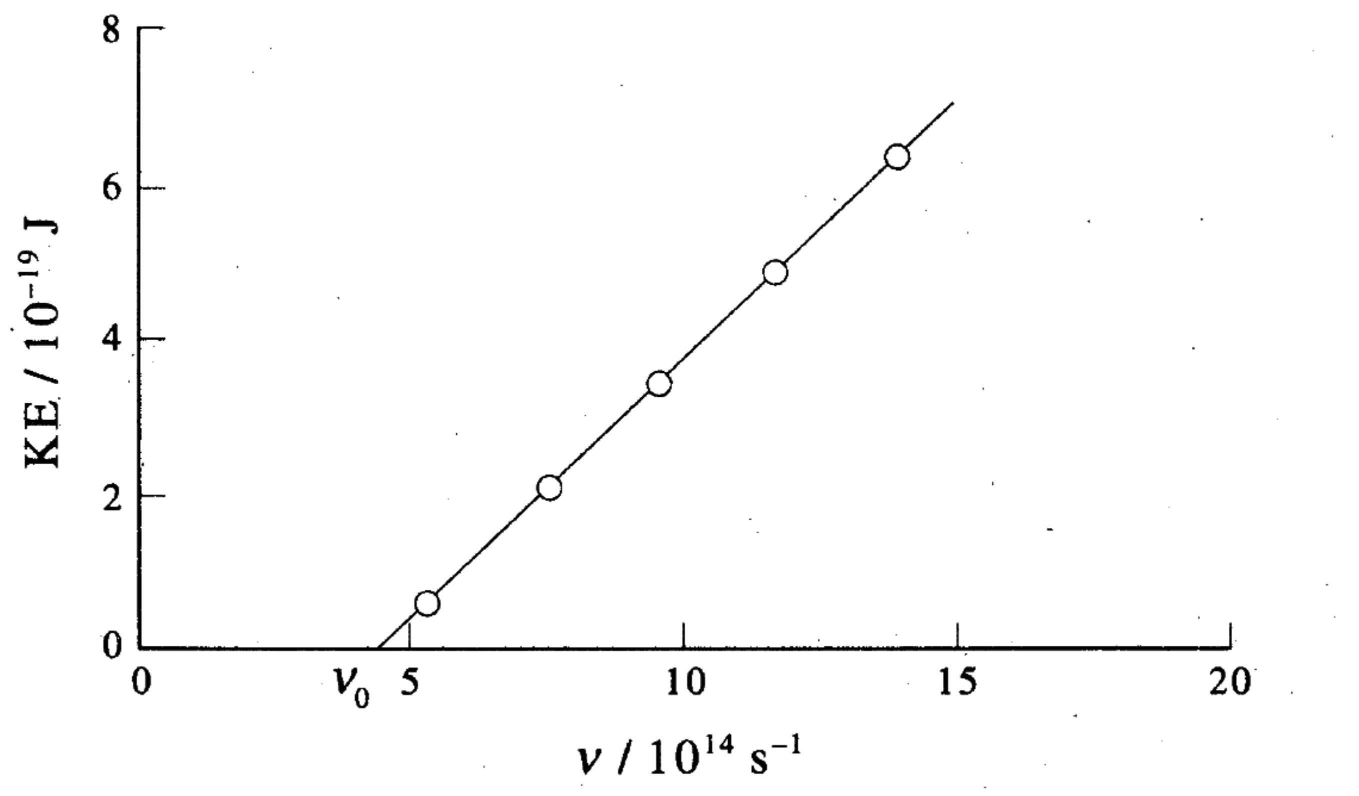

FIGURE 1.4
The kinetic energy of electrons ejected from the surface of sodium metal versus the frequency of the incident ultraviolet radiation. The threshold frequency here is 4.40×10^{14} Hz (1 Hz = 1 s^{-1}).

$$KE = \frac{1}{2}mv^2 = h\nu - \phi$$

$$\phi = h\nu_0$$

Then, what is light? Is it a particle or a wave? Nowadays, we assume that light has *particle-wave duality*. Photoelectric effect shows particle-like nature of light, meanwhile interferece experiment shows the wave-like nature of light.

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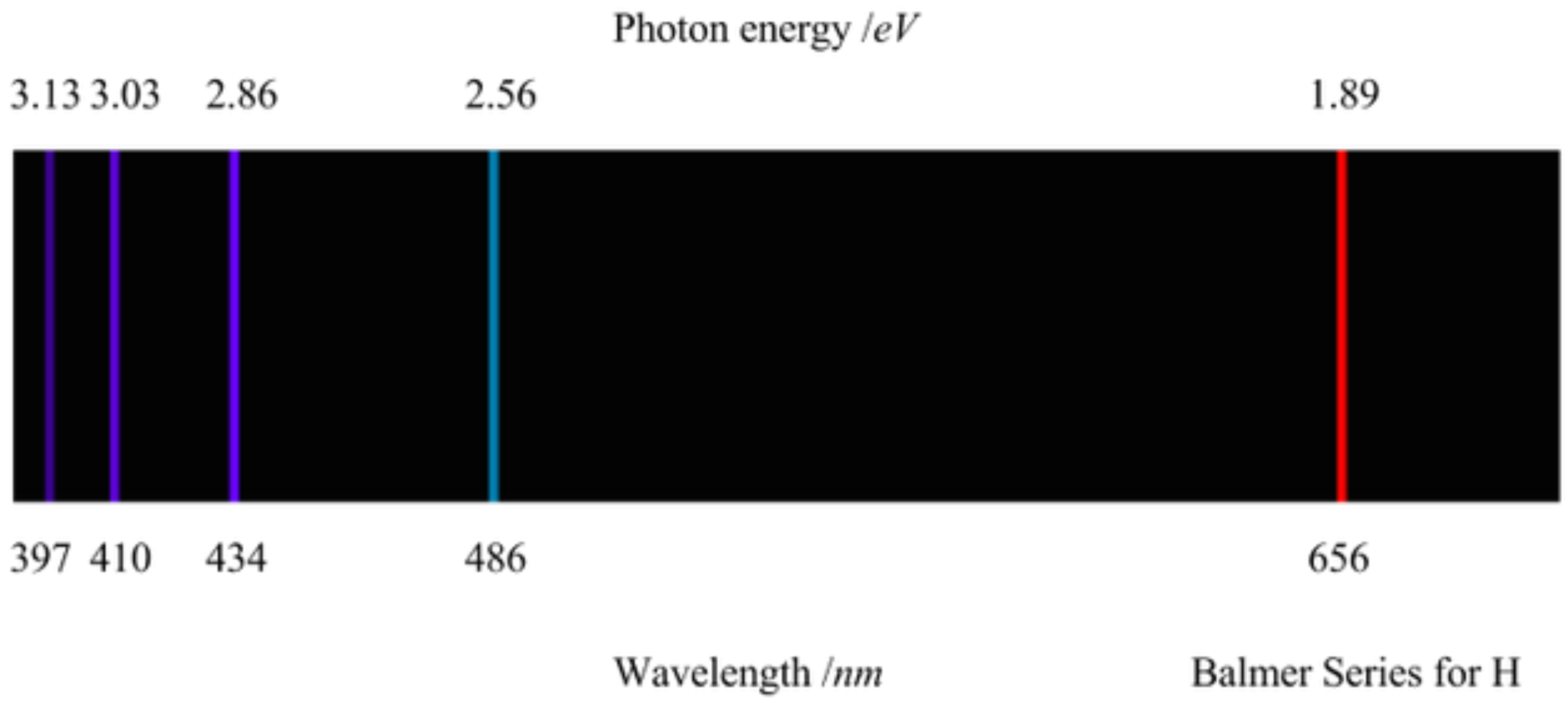
Hydrogen Atomic Spectrum

Each atom has a characteristic *emission spectrum*. Since emission spectrum consists of only certain discrete frequencies, they are called *line spectrum*.



In 1885, Johann Balmer found the regularity in the hydrogen emission spectrum.

$$\tilde{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad (n = 3,4,\ldots)$$

Where $R = 109680\,\mathrm{cm}^{-1}$ (Rydberg constant). But he did not figure out why the wavelength has such formula.

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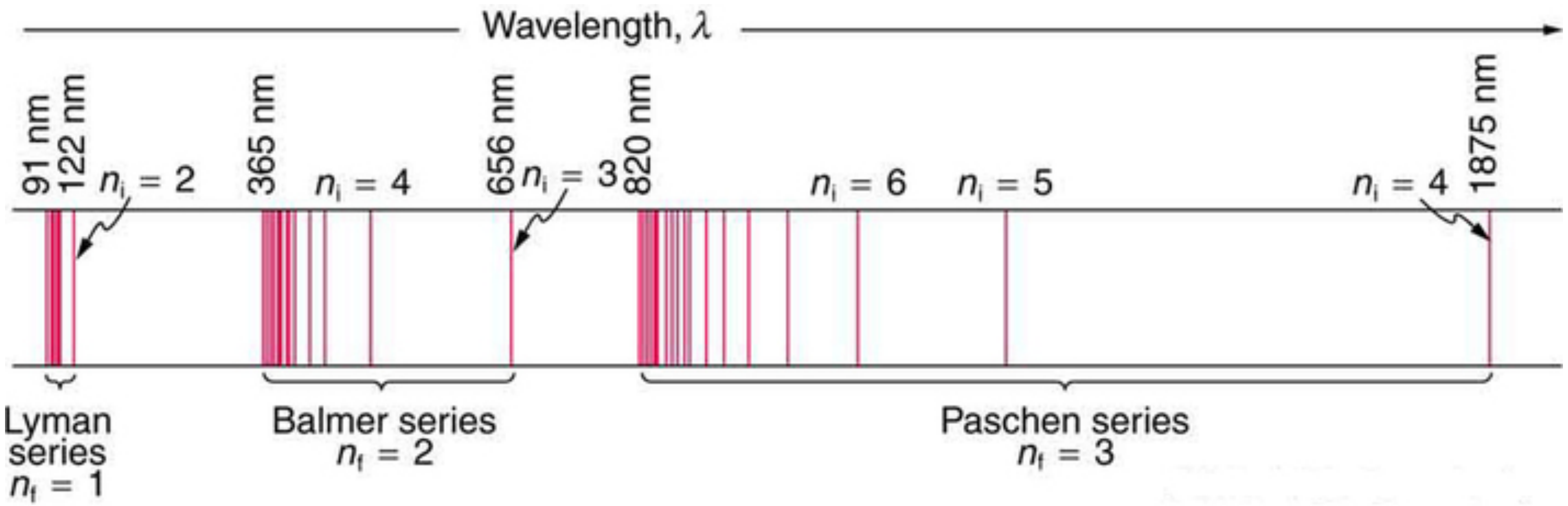
Hydrogen Atomic Spectrum

In general, Balmer's formula can be extended to Rydberg's formula.

$$\tilde{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad (n_1, n_2 = 1,2,\ldots)$$

The Rydberg formula accounted for all the lines in the hydrogen atomic spectrum.



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Matter Waves

In 1924, Louis de Broglie postulated that *matter might also display wavelike properties*.

Einstein had shown that the wavelength and the momentum of photon are related by

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

De Broglie argued that both light and matter obey this equation, predicted that a particle of mass *m* moving with a velocity *v* has a *de Broglie wavelength*.

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

Later, de Broglie waves were observed experimentally, with *electron diffraction* experiment.

We use X-ray diffraction for determining structure of solids, usually.

X-ray is light; therefore it exhibits wave-like property, diffraction.

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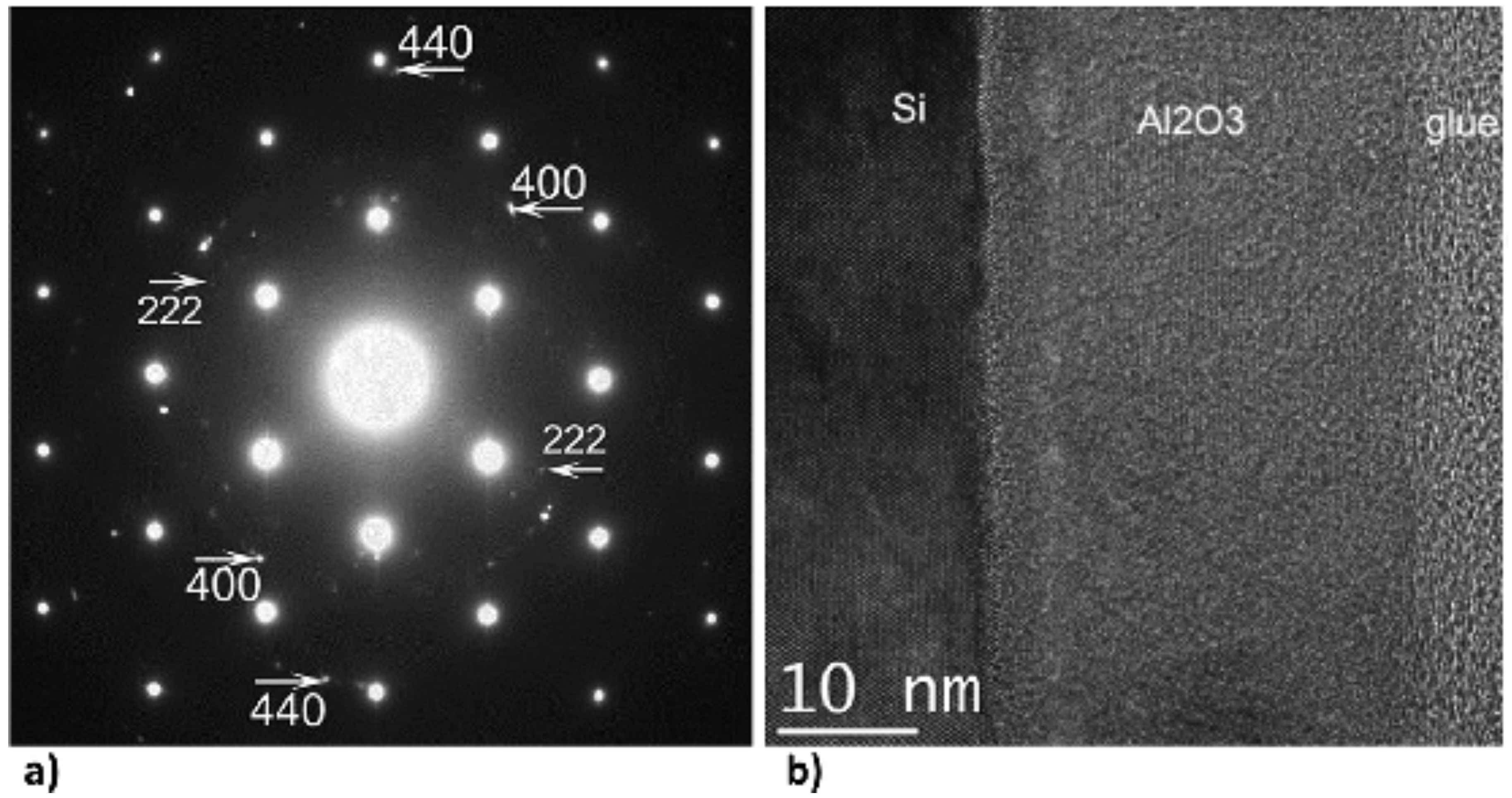
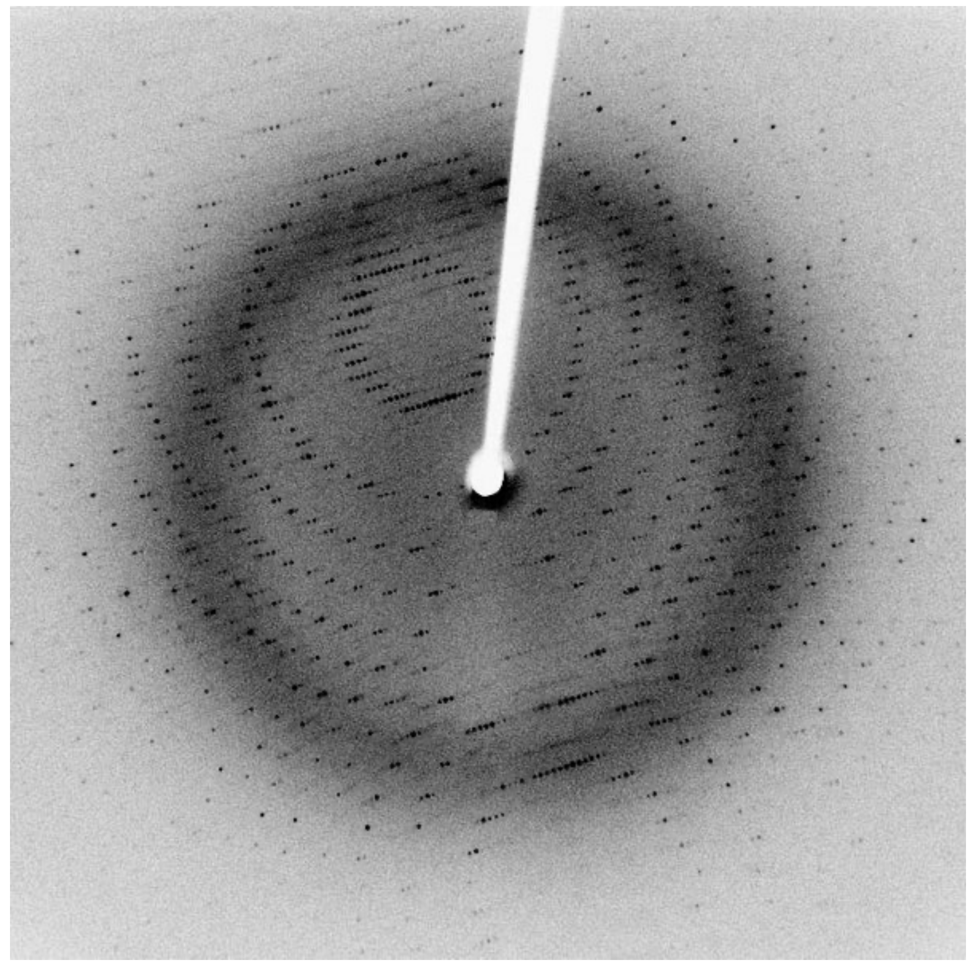
Matter Waves

By repeating the experiment with electron, we yield similar pattern with diffraction.

Truly, electron has *wave-like* nature!



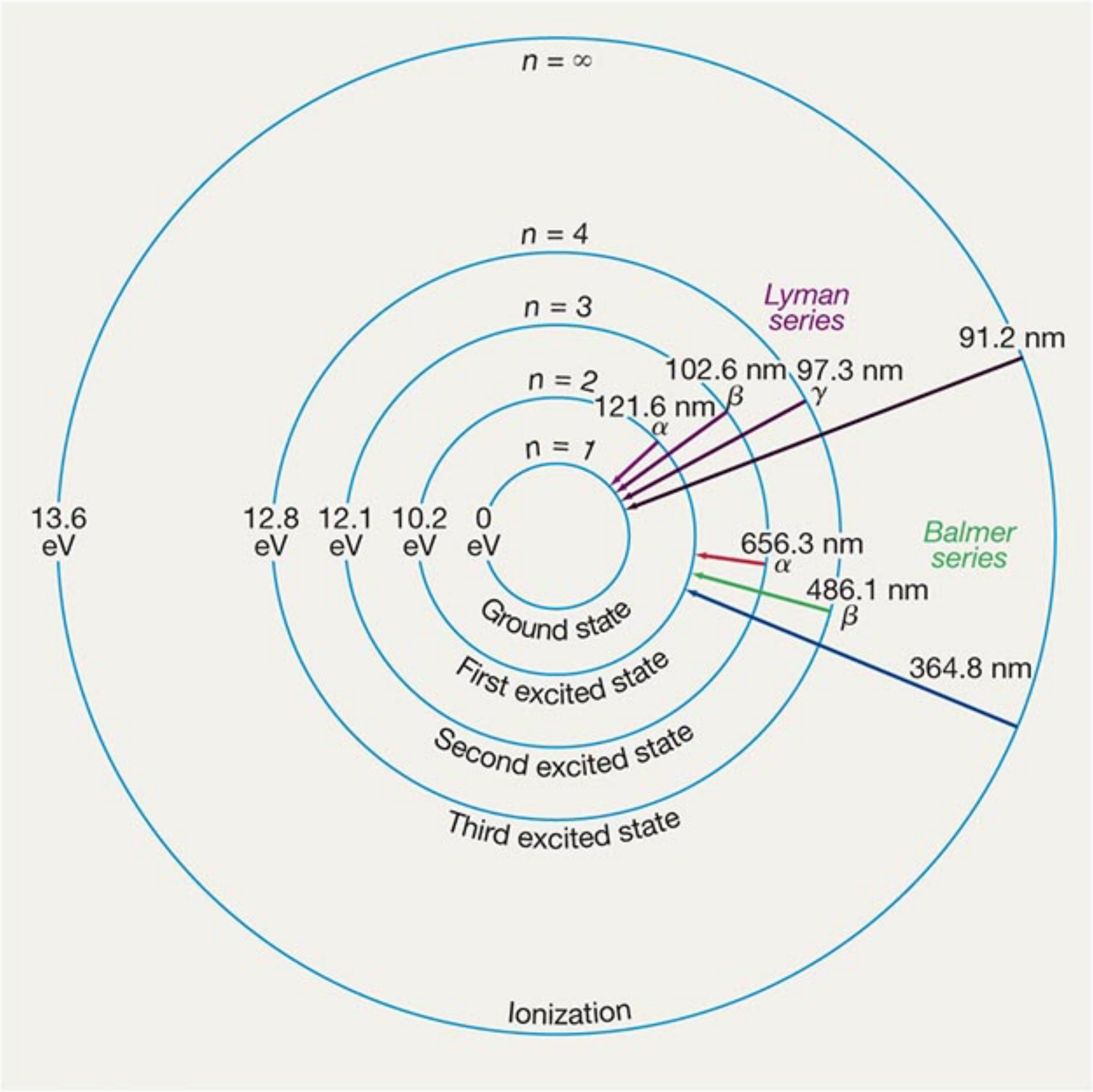
Electron diffraction pattern of aluminum oxide



X-ray diffraction pattern

Bohr Model

Before we start, note that Bohr model is errornous model.



Assumption of Bohr model

Quantized orbits. Electrons possess particular orbit around the nucleus. Condition for the orbit is called *angular momentum quantization*.

$$L = m_e v r = n\hbar \ (n = 1,2,3,\ldots)$$

Frequency condition. Electrons can 'jump' from one orbit to another orbit. In this transition process, electron emits or absorbs photon with energy corresponding to the difference of energy between two allowed orbits.

$$\Delta E = h\nu$$

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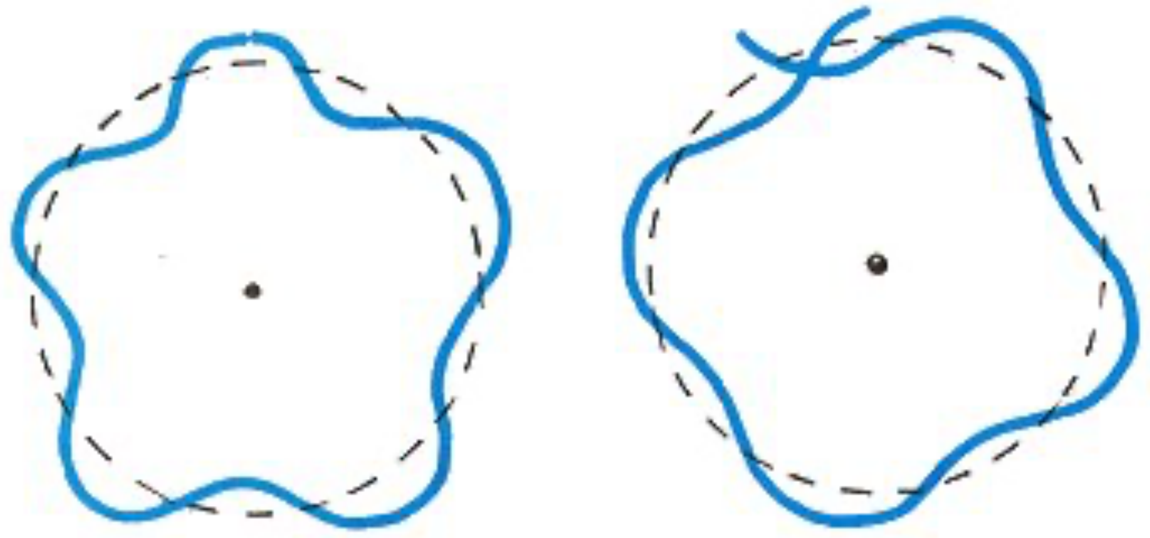
Standing wave condition

For the stable (or *allowed*) orbit, matter wave of electron should form *standing wave* along the orbit.

Otherwise, matter wave of electron will undergo *destructive interference*; therefore electron should be in certain quantized orbits.



$$2\pi r = n\lambda \ (n = 1,2,3,\ldots)$$

$$\Longrightarrow \quad 2\pi r = n\frac{h}{mv}, \quad mvr = n\frac{h}{2\pi} = n\hbar$$

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Bohr Model

The *coulombic force* of attraction between the proton and the electron is balanced by the *centrifugal force*:

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

By substituting $m_e vr = n\hbar$, we obtain

$$r = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} n^2 \quad (n = 1,2,\ldots)$$

In case of $n = 1$, we call it as *Bohr radius*.

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \simeq 0.053\,\mathrm{nm}, \quad r = n^2 a_0 \quad (n = 1,2,\ldots)$$

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Bohr Model

From the energy formula, we can calculate *quantized* energy level of hydrogen atom.

$$E = E_K + E_V = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} \quad (n = 1,2,\ldots)$$

We call $n = 1$ state as a *ground state*. From the frequency condition, allowed energy differences are

$$\Delta E = \frac{m_e e^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu$$

This equation coincides with Rydberg equation; therefore Bohr model can explain the hydrogen atomic spectrum completely.

However, Bohr model is invalid in many-electron case.

Moreover, it contradicts to classical law of electrodynamics.

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Uncertainty Principle

Heisenberg's uncertainty principle is a fundamental principle of nature.

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

Here, Δx and Δp denotes the uncertainty in position and momentum, respectively.

Qualitative explanation

To observe electron, we need light (photon). Note that resolution of observation is related to λ.

If we use photon with high *p* (small λ), we can reduce Δx.
However, from the momentum conservation, we cannot know what was exact *p* of electron.
Therefore, Δp increases.

If we use photon with small *p*, Δp may decrease.
However, since the size of electron is smaller than the resolution, we cannot know the location of electron: larger Δx.

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