

Quantum Mechanics

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1 Origins of Quantum Mechanics

- Blackbody radiation
- Photoelectric effect



- Quantum mechanics was born in early 20th century
due to collapse of deterministic classical mechanics
driven by Euler-Lagrange equations
- Collapse resulted from the discovery of various phenomena
which are inexplicable with classical physics
- Pathway to quantum mechanics invariably begins with Planck
and his analysis of blackbody spectral data

Stefan-Boltzmann law

- Rate at which objects radiate energy $\Rightarrow L \propto AT^4$
- At normal temperatures $\Rightarrow \approx 300$ K
not aware of this radiation because of its low intensity
- At higher temperatures \Rightarrow sufficient IR radiation to feel the heat
- At still higher temperatures $\Rightarrow \mathcal{O}(1000$ K)
objects actually glow such as a red-hot electric stove burner
- At temperatures above 2000 K
objects glow with a yellow or whitish color \Rightarrow filament of lightbulb
- Blackbody \Rightarrow idealized object that absorbs all incident radiation regardless of frequency or angle of incidence
- bolometric luminosity: $L = \sigma A T^4 \Rightarrow \sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
- Radiant flux \Rightarrow total power leaving 1 m^2 of blackbody surface @ T

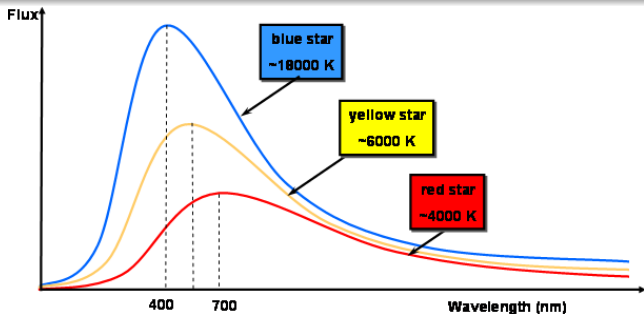
$$F(T) = L/A = \sigma T^4 \quad (1)$$

Wien's displacement law

- Wavelength λ_{\max} at which spectral emittance reaches maximum decreases as T is increased in inverse proportion to T

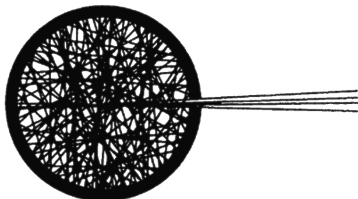
$$\lambda_{\max} T = 2.90 \times 10^{-3} \text{ m K} \quad (2)$$

- Qualitatively consistent with observation that heated objects first begin to glow with red color and at higher temperatures color becomes more yellow



Approximate realization of blackbody surface

- Consider hollow metal box with walls in thermal equilibrium @ T
- Cavity is filled with radiation forming standing waves
- Suppose there is small hole in one wall of box
which allows some radiation to escape
- It is the hole and not the box itself that is the blackbody
- Radiation from outside that is incident on hole gets lost inside box and has a negligible chance of reemerging from the hole
no reflections occur from blackbody (the hole)
- Radiation emerging from hole \rightarrow sample of radiation inside box



Radiation inside box

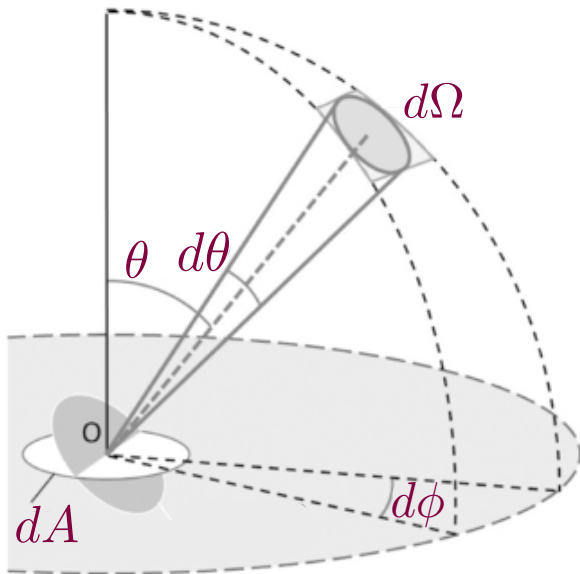
- $u(T)$ ⇨ energy density (energy per unit volume) [J m^{-3}]
- $\frac{du}{d\lambda} \equiv u_\lambda(\lambda, T)$ ⇨ spectral energy density [$\text{J m}^{-3} \text{nm}^{-1}$]
- If we look into interior of box and measure spectral energy density with wavelengths between λ and $\lambda + d\lambda$ in small volume element result would be ⇨ $u_\lambda(\lambda, T) d\lambda$

Surface brightness (or spectral emittance)

- $B_\lambda(\lambda, T)$ ⇨ spectral radiant flux per steradian emitted from unit surface that lies normal to view direction
- Because photons of all wavelengths travel at c wavelength dependence of u_λ equals that of B_λ
- It does not matter whether radiation sampled is: that in 1 m^3 @ fixed time or that impinging on 1 m^2 in 1 s

$$B_\lambda(\lambda, T) = \frac{c}{4\pi} u_\lambda(\lambda, T) \quad (3)$$

Surface element \Rightarrow different for each view direction



Radiant flux through unit area of fixed surface immersed in blackbody

$$dF_\lambda(\lambda, T) = B_\lambda(\lambda, T) \cos \theta d\Omega \quad (4)$$

$$F(T) = \int_0^\infty \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} B_\lambda(\lambda, T) \frac{dA \cos \theta}{dA} d\Omega d\lambda \quad (5)$$

$$\int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \cos \theta \sin \theta d\theta d\phi = \pi \quad (6)$$

$$F(T) = \int_0^\infty B_\lambda(\lambda, T) d\lambda = \sigma T^4 \quad (7)$$

$$u(T) = \int_0^\infty u_\lambda(\lambda, T) d\lambda = a T^4 \quad (8)$$

$$a = 4\sigma/c = 7.566 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$$

- Wave can be characterized by:
wavelength λ , speed c , period $T = \lambda/c$, frequency $\nu = 1/T = c/\lambda$

$$\omega = 2\pi\nu = 2\pi c/\lambda \quad (9)$$

- Spectral energy density within $(\lambda, \lambda + \Delta\lambda)$

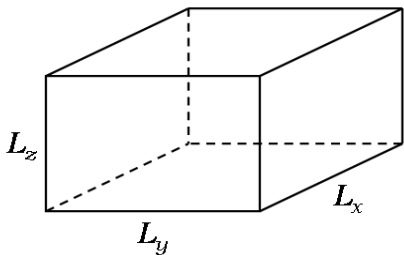
$$u_\lambda(\lambda, T) d\lambda = u_\omega(\omega, T) d\omega \quad (10)$$

- (9) and (10) yield

$$u_\lambda(\lambda, T) = u_\omega(\omega, T) \left| \frac{d\omega}{d\lambda} \right| = u_\omega(\omega, T) \frac{2\pi c}{\lambda^2} \quad (11)$$

- Consider box in thermal equilibrium @ T
- Spectral energy density of radiation with frequencies between ω and $\omega + d\omega$ in small volume element

$$\underbrace{u_\omega(\omega, T)}_{\substack{\text{average energy} \\ \text{per } \omega \text{ interval} \\ \text{per volume}}} d\omega = \left(\underbrace{\frac{\text{number of states inside box} \\ \text{within interval } (\omega, \omega + d\omega)}{\text{volume of the box}}}_{N(\omega, T)} \right) \cdot \left(\underbrace{\text{average energy} \\ \text{of one radiation} \\ \text{mode of frequency } \omega}_{\langle E \rangle} \right)$$



$$\Rightarrow V = L_x L_y L_z$$

Estimate of $N(\omega, T)$

- Take $Z(\omega)$ \Rightarrow # of standing waves up to ω in box

$$\left(\begin{array}{l} \text{number of states inside the box} \\ \text{within the interval } (\omega, \omega + d\omega) \end{array} \right) = \frac{dZ}{d\omega} d\omega \quad (12)$$

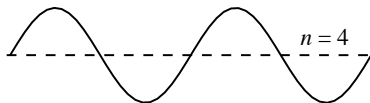
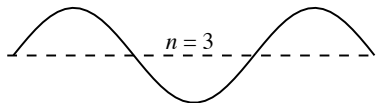
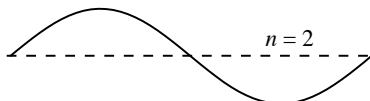
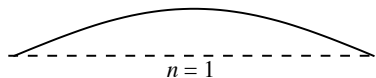
- Assume allowed frequencies of the radiation are spaced evenly

$$Z(\omega) = \underbrace{\varkappa \left(\frac{\omega}{\omega_{\min,x}} \right)}_{\substack{\text{number of waves} \\ \text{in } x \text{ direction}}} \underbrace{\left(\frac{\omega}{\omega_{\min,y}} \right)}_{\substack{\text{number of waves} \\ \text{in } y \text{ direction}}} \underbrace{\left(\frac{\omega}{\omega_{\min,z}} \right)}_{\substack{\text{number of waves} \\ \text{in } z \text{ direction}}}$$

- Minimum frequency exists because there is maximum wavelength

$$\lambda_{\max,x} = 2L_x \quad (13)$$

that can exist between walls located L_x units apart



$$\omega_{\min,j} = \frac{2\pi c}{2L_j} = \frac{\pi c}{L_j} \quad j = \{x, y, z\} \quad (14)$$

- Next 3 wavelengths $\Rightarrow 2L_x/2, 2L_x/3, 2L_x/4$
- Corresponding frequencies $\Rightarrow 2\omega_{\min,x}, 3\omega_{\min,x}, 4\omega_{\min,x}$
- This justifies our assumption
that frequencies of radiation in box are spaced evenly

- Using (14)

$$Z(\omega) = \varkappa \frac{\omega^3}{(\pi c)^3 / (L_x L_y L_z)} = \varkappa \frac{\omega^3}{(\pi c)^3} L_x L_y L_z \quad (15)$$

- Photons have two independent polarizations $\Rightarrow \varkappa = \pi/3$
(2 states per wave vector $\vec{k} = (\omega/c) \hat{n}$ propagating in direction \hat{n})
- From (15)

$$\left(\begin{array}{l} \text{number of states inside the box} \\ \text{within the interval } (\omega, \omega + d\omega) \end{array} \right) = \frac{\omega^2}{\pi^2 c^3} L_x L_y L_z$$

and finally

$$\frac{\left(\begin{array}{l} \text{number of states inside the box} \\ \text{within the interval } (\omega, \omega + d\omega) \end{array} \right)}{\text{volume of the box}} = \frac{\omega^2 d\omega}{\pi^2 c^3} \quad (16)$$

- Energy of each standing wave (normal mode) distributed according to Maxwell-Boltzmann distribution

$$P(E) dE = \frac{e^{-E/kT}}{kT} dE \quad (17)$$

$k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ ☞ Boltzmann's constant

- Classical Rayleigh-Jeans prediction

$$\langle E \rangle = \frac{\int_0^\infty P(E) E dE}{\int_0^\infty P(E) dE} = \dots = kT \quad (18)$$

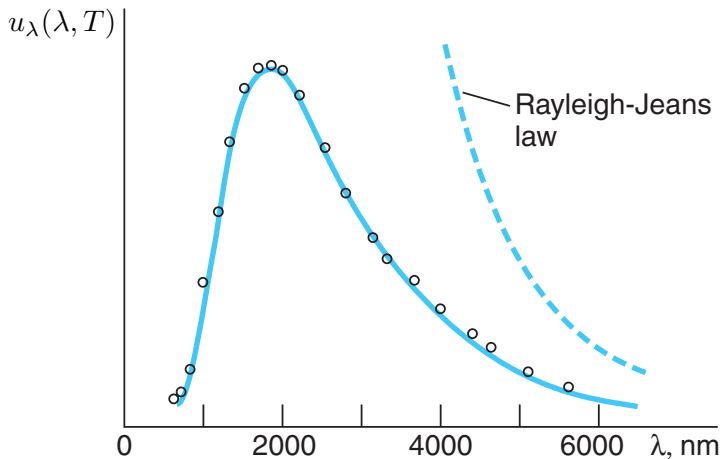
- Energy density and surface brightness become

$$u_\lambda(\lambda, T) d\lambda = \frac{N(\lambda) d\lambda}{V} kT = \frac{8\pi}{\lambda^4} kT d\lambda \quad (19)$$

and

$$B_\lambda(\lambda, T) = \frac{c}{4\pi} u_\lambda(\lambda, T) = \frac{2c}{\lambda^4} kT \quad (20)$$

UV catastrophe



$$\int_0^{\infty} u_\lambda(\lambda T) d\lambda \rightarrow \infty \quad (21)$$

At short wavelengths classical theory is absolutely not physical

Planck proposed a solution to this problem...

- Energy is *not* a continuous variable
- Each oscillator emits or absorbs only in integer multiples $\Delta E = h\nu$

$$E_n = n \Delta E, \quad \text{with } n = 0, 1, 2, 3, \dots \quad (22)$$

$h = 6.626 \times 10^{-34} \text{ J s} = 4.136 \times 10^{-15} \text{ eV s}$ Planck's constant

- Average energy of an oscillator is then given by the discrete sum

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} E_n P(E_n)}{\sum_{n=0}^{\infty} P(E_n)} = \dots = \frac{hc/\lambda}{e^{hc/(\lambda kT)} - 1} \quad (23)$$

- Multiplying this result by number of oscillators per unit volume
 ☞ spectral emittance distribution function of radiation inside cavity

$$B_\lambda(\lambda, T) = \frac{2c}{\lambda^4} \langle E \rangle = \frac{2c}{\lambda^4} \frac{hc/\lambda}{e^{hc/(\lambda kT)} - 1} \quad (24)$$

Relevant limits

- Classical limit $h \rightarrow 0$ and $\Delta E \rightarrow 0$ \Rightarrow For $x = hc/(\lambda kT) \ll 1$ exponential in (24) can be expanded using $e^x \approx 1 + x + \dots$

$$e^{hc/(\lambda kT)} - 1 \approx \frac{hc}{\lambda kT} \quad \text{and so } \langle E \rangle = \frac{hc/\lambda}{e^{hc/(\lambda kT)} - 1} = kT \quad (25)$$

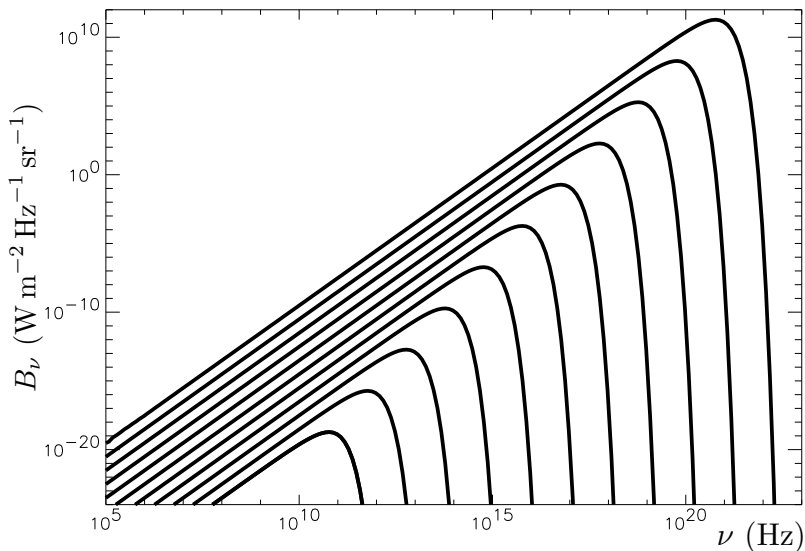
- For long wavelength \Rightarrow Rayleigh-Jeans formula

$$\lim_{\lambda \rightarrow \infty} u_\lambda \rightarrow \frac{8\pi}{\lambda^4} kT \quad (26)$$

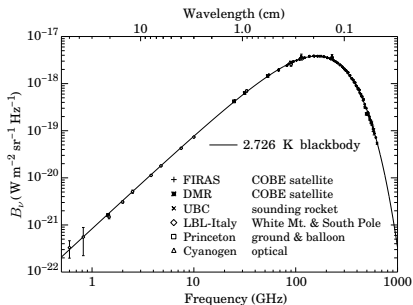
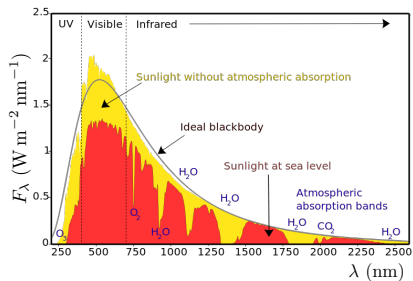
- Quantum regime $\lambda \rightarrow 0$ (i.e. high photon energy)
 $e^{hc/(\lambda kT)} \rightarrow \infty$ exponentially faster than $\lambda^5 \rightarrow 0$ so

$$\lim_{\lambda \rightarrow 0} \frac{1}{\lambda^5 (e^{hc/(\lambda kT)} - 1)} \rightarrow 0 \quad (27)$$

There is no ultraviolet catastrophe in the quantum limit !!!

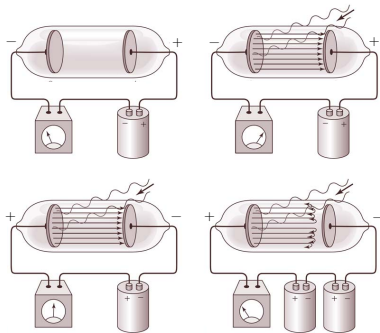
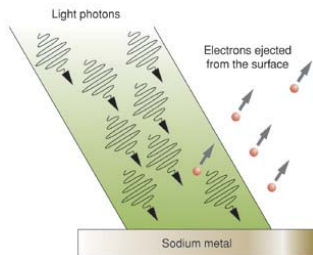
Planck spectrum of blackbody radiation for 10^0 K, 10^1 K, \dots , 10^{10} K

Specific examples: the Sun and the CMB



- Success of Planck's idea immediately raises question:
why is it that oscillators in walls
can only emit and absorb energies in multiples of $h\nu$?
- Explanation supplied by Einstein:
light is composed of particles called photons
and each photon has an energy $E_\gamma = h\nu$
- Photoelectric effect is the observation that a beam of light
can knock electrons out of metal surface
- Electrons emitted from surface are called photoelectrons
- What is surprising about photoelectric effect?
Energy of photoelectrons independent of intensity of incident light
- If frequency of light is swept
find minimum frequency ν_0 below which no electrons are emitted
- Energy $\varphi = h\nu_0$ corresponding to this frequency
is called work function of surface

- Beam of light can knock electrons out of metal surface
- Photoelectrons collected on detector which forms part of electrical circuit
- Current measured in circuit
 \propto # electrons striking detector plate
- To measure kinetic energy of e^- 's
apply static retarding potential V
- Only electrons with $K > eV$
will reach the plate
- Any electrons with $K < eV$
will be repelled and won't be detected



Why classical electromagnetism fails to explain photoelectric effect

In classical electromagnetism...

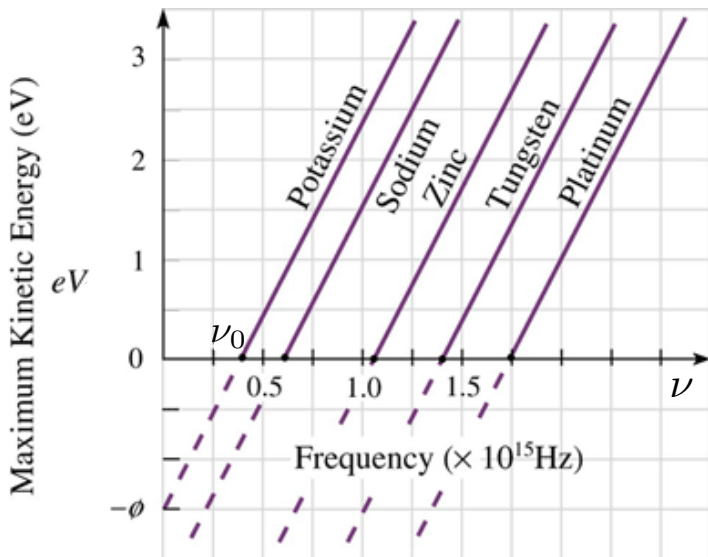
- Increasing intensity I of beam
 increases amplitude of oscillating electric field \vec{E}
 Since force incident beam exerts on electron is $\vec{F} = e\vec{E}$
 theory predicts photoelectron energy increases with increasing I
 However $\Rightarrow V_0$ is independent of light intensity
- As long as intensity of light is large enough
 photoelectric effect should occur at any frequency
 in direct contradiction with experiment
 showing clear cutoff ν_0 below which no electrons are ejected
- Energy imparted to e^- must be “soaked up” from incident wave
 if very weak light is used \Rightarrow expected measurable time delay
 between light striking surface and e^- emission
 This has never been observed

Why all problems are solved by quantum mechanics

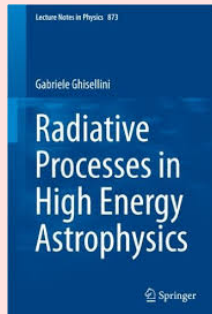
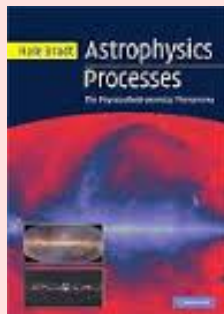
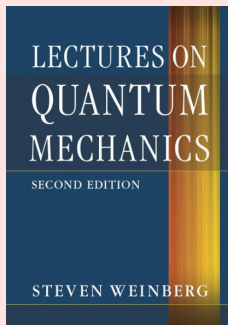
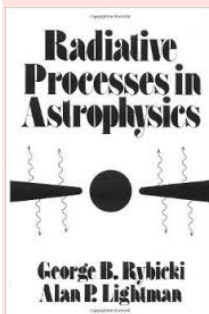
In quantum mechanics...

- 1 Doubling intensity doubles number of photons
but doesn't change their energy
total number of photons striking surface
is immaterial in determining energy of ejected electron
- 2 Frequency of light determines photon energy
photons with $h\nu < \phi$ don't have enough energy to leave surface
- 3 Photoelectric effect is viewed as single collisional event
and no time delay is predicted
- 4 When K_{\max} is plotted as function of frequency $\nu > \nu_0$
experimental data fit straight line whose slope equals h

$$K_{\max} = h\nu - \phi$$



Bibliography



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