Chemistry 331
Introduction to Quantum Chemistry

Instructor: Derek Leaist (dleaist@stfx.ca), Office PSC 3072, Lab PSC 3020

Lectures: Monday 11:15 am, Tuesday 1:15 pm, Thursday 12:15 pm (PSC 3046)

Tutorials: Wednesday 2:15 pm (AX 23A)

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General Description: Chemistry 331 introduces the basic ideas and applications of quantum theory, quantum chemistry, and statistical mechanics, emphasizing energy levels and how they are occupied. The postulates of quantum mechanics are developed and used to solve a variety of problems, including thermal radiation, confined particles, free particles, molecular vibration, molecular rotation, and atomic orbitals, with spectroscopic and other applications. The methodology and interpretive nature of quantum mechanics are stressed and the connection between theory and experiment is emphasized.

Prerequisite: Chemistry 232

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Course Notes: pdf copies provided

Textbook: pdf copies of textbooks available

Assignments: About eight problem sets will be assigned to cover the course material.

Term Tests: **Wednesday 13 October, 1:15 – 5:00 pm, AX 23A**
Wednesday 24 November, 2:15 – 5:00 pm, AX 23A

Final Exam: TBA (in the Christmas exam period)

Office Hours: Mon. 9:30 to 10:30 am, Tues. 11:30 am to 12:30 pm, Fri. 1:00 to 2:00 am

Course Outline

1. **Brief Summary of Classical Mechanics:** Newton's Laws. Hamilton's equations of motion. Other coordinate systems. Math review.

2. **The Need for Quantum Mechanics:** Failures of classical mechanics. Thermal radiation. Low-temperature heat capacities. Photoelectric effect. Atomic spectra. De Broglie relation. Electron diffraction. Wave nature of matter. The uncertainty principle.

3. **Postulates of Quantum Mechanics:** Connection between classical and quantum mechanics. The postulates or laws of quantum mechanics. Stationary states.

4. **Some One-Dimensional Solutions:** The free particle problem. Particle-in-a-box problem. Beam-potential barrier problems. Quantum mechanical tunneling. Applications.

5. **Important Theorems:** Commutators. Self-adjoint or Hermitian operators. Quantum numbers. Examples.

6. **One-Dimensional Harmonic Oscillator:** Raising and lowering operators. Energy levels and wave functions. Properties of the oscillator. Transition selection rules. Zero-point energy. A model for a vibrating molecule. Vibrational spectroscopy and diatomic molecules. Other applications.

7. **Multi-Dimensional Problems:** Three-dimensional free particle, particle-in-a-box, and harmonic oscillator problems. Degenerate energy levels. Applications.

8. **Multi-Dimensional Problems with Spherical Symmetry:** Quantum numbers and general method for the solving the problems. The angular parts of atomic orbitals. *The Harmonic Oscillator and the Rigid Rotator:* Model for a rotating molecule; rotational spectroscopy of diatomic molecules; selection rules; bond lengths; vibrational-rotational spectra; electronic-vibrational-rotational spectra. *The Hydrogen Atom:* The radial and angular parts of the wave functions for the one-electron atom and ion; energies; spectra and selection rules; average values of properties; total probability and radial distribution functions; radius of the atom; probability density plots; directed atomic orbitals.

Course Notes available on the Chem 331 Moodle pages

and at: **https://people.stfx.ca/dleaist/Chem331/**

Chemistry 331 Course Schedule (2021)

Classes: Tuesday 07 September to Tuesday 07 December
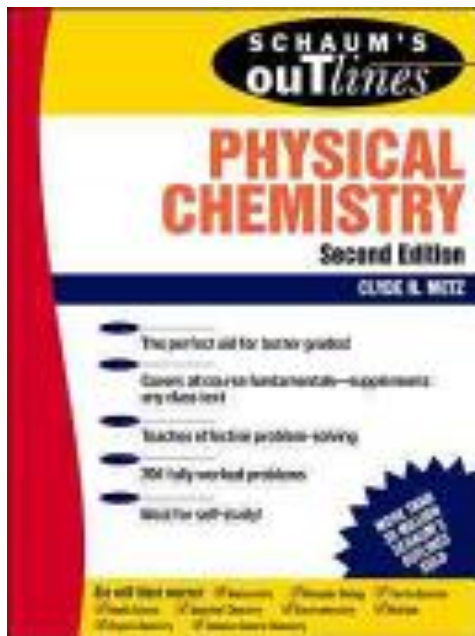
Tutorials: **15 September** (Blocks HG/JH, Wednesdays 2:15 to 5:00 pm, AX 23A)
29 September
06 October
03 November
17 November
01 December

Term Tests: **Wednesday 13 October**, **2:15 pm to 5:00 pm**, AX 23A
Wednesday 24 November, **2:15 pm to 5:00 pm**, AX 23A

Final Exam: **TBA** (in the Christmas final exam period)

Course Mark

Final Exam	45 %
Term Tests	40 %
Assignments	15 %

Schaum's Outline of Physical Chemistry

2nd edition ($25 Amazon.ca)

Clyde A. Metz

Chapters on quantum mechanics and spectroscopy, also thermodynamics, electrochemistry, kinetics, and transport properties.

  concise summaries and worked problems.

Pdf versions of physical chemistry textbooks with chapters on quantum mechanics and spectroscopy are available <u>online</u>. Examples:

Physical Chemistry, 3rd Edition, Engel and Reid
https://www.academia.edu/people/search?utf8=%E2%9C%93&q=quantum+chemistry+Engel+Reid

Physical Chemistry, 4th Edition, Bawendi, Alberty and Silbey
http://www.slideshare.net/abahanaskasmui/physical-chemistry-4th-bawendi-alberty-silbey-library-pirate
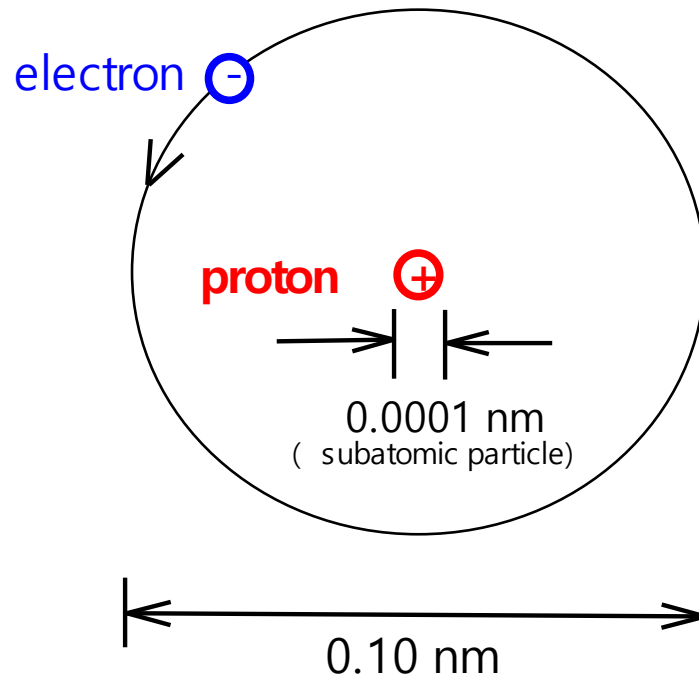
Physical Chemistry, Moore
https://ia802302.us.archive.org/18/items/physicalchemistr029701mbp/physicalchemistr029701mmb.pdf

Why do we need "quantum" mechanics? What's wrong with classical Newtonian mechanics?   *An important chemical example* :

Hydrogen Atom

electron and a proton

(ground-state diameter about 0.10 nm)

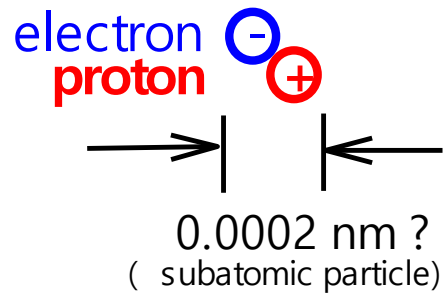electron ⊖

proton ⊕

0.0001 nm
(subatomic particle)

0.10 nm

Ok. But **why doesn't the electron spiral inwards and merge with the proton**, forming a **subatomic particle** (diameter << 0.10 nm for H atoms)?

Hydrogen Atom

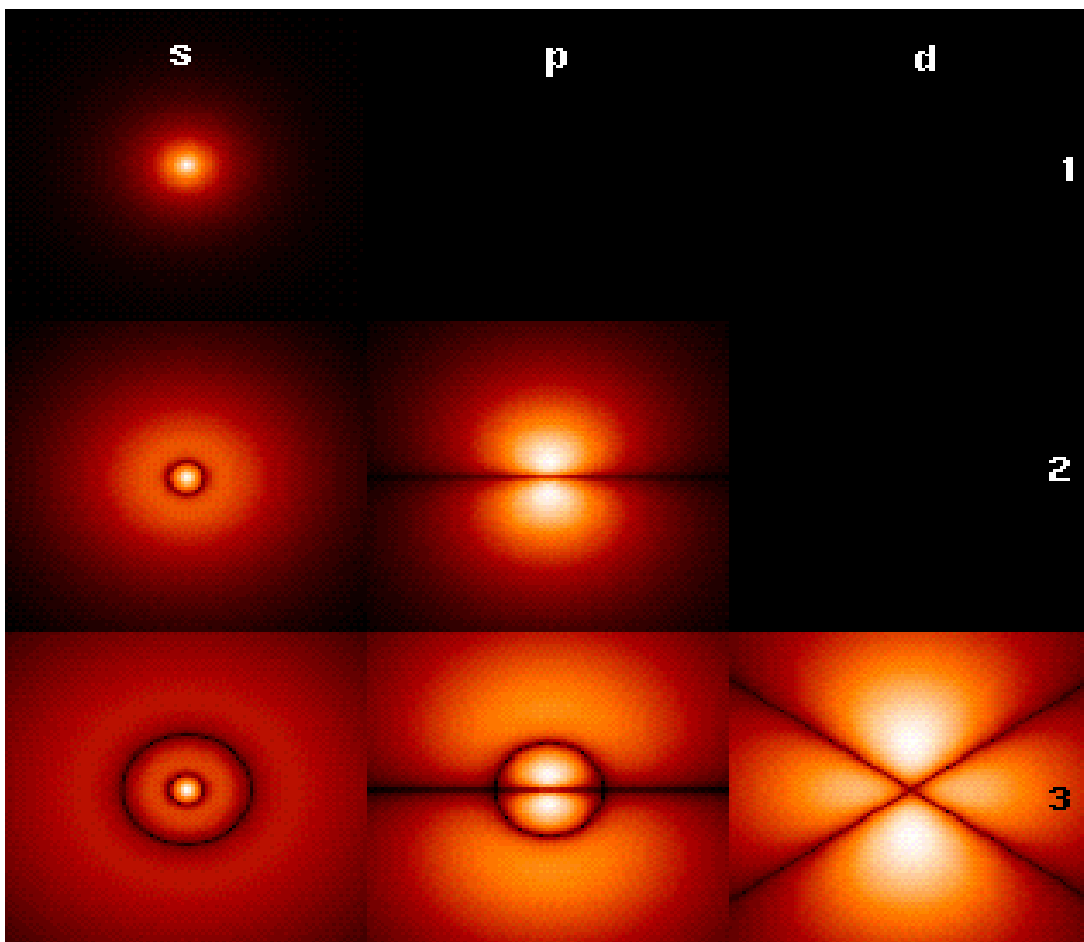electron and a proton

positive and negative charges attract, so:

electron ⊖
proton ⊕

0.0002 nm ?
(subatomic particle)

Why do we need "quantum" mechanics? What's wrong with classical Newtonian mechanics? *Another important chemical example* :

Orbitals　　Example: 1s for the ground state hydrogen atom

But what are orbitals?

Historical Development of Quantum Mechanics

At the end of the 1800s, many physicists believed that all principles of physics had been discovered. There were "gaps", such as the way radiation interacts with matter, but these were felt to be "just details".

"*Classical*" Physics

- Newton's Laws and classical mechanics
- Classical Thermodynamics
- Optics, electricity, magnetism

$$\vec{F} = m\vec{a}$$

$$= m\frac{d^2\vec{r}}{dt^2}$$

Key ideas of classical physics

- continuous observables

- no restriction on the energy of systems

- ***determinism*** – Everything about a system's future is known by solving for $r(t)$ from Newton's second law.

- wave nature of light

The Nature of Light

1801   Thomas Young provided convincing experimental evidence for the wave nature of light. Diffraction and interference patterns were observed.

interference pattern observed with Young's double slit experiment
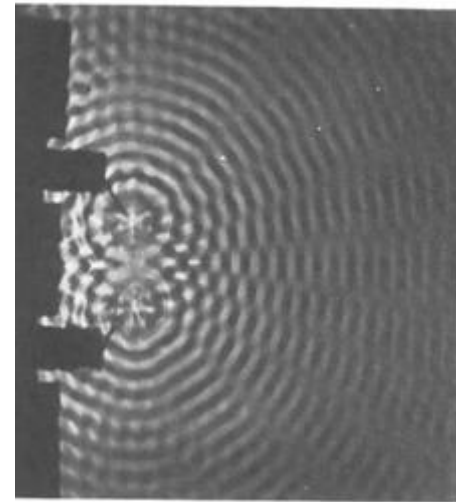
equivalent interference pattern from waves of water

1860s   Maxwell developed four equations that unified the laws of electricity and magnetism. The speed of an electromagnetic wave predicted was the same as the speed of light that was experimentally measured.

Light was concluded to be an electromagnetic wave.

The Physics of Chemistry was not as Well Developed

- The existence of nuclei and electrons was known.

- Most of the periodic table had been developed (empirically).

- Catalogs of chemical reactions were available.

- The nature of molecules and chemical bonds were "gaps" in our knowledge.

By the beginning of the 1900s, several worrisome experimental observations could *not* be explained by classical physics!

The 'small gaps' turned into fundamental problems with classical physics and a radical new theory was needed to solve them.
A revolution was brewing!

Five Key Observations that 'Violated' Classical Physics

Several key experimental observations could **not** be explained by classical physics led to the development of quantum mechanics.

> **1. <u>Blackbody Radiation</u>** - *disobeyed classical electromagnetic theory*

One of the most important observed phenomena (from a historical point of view) that made scientists question classical mechanics was blackbody radiation.

What is blackbody radiation (also called thermal radiation)?

All materials:

- continually absorb and give off radiation
- in everyday experience, most radiation is emitted as ***infrared***

As materials are heated to higher temperature, the radiation emitted shifts toward higher frequencies.

*red hot < white hot < blue hot*
(*why?*)

What is blackbody (thermal) radiation?

An object is a blackbody if it absorbs all incident radiation but reflects none, at all frequencies. The radiation emitted by a blackbody is called blackbody radiation.
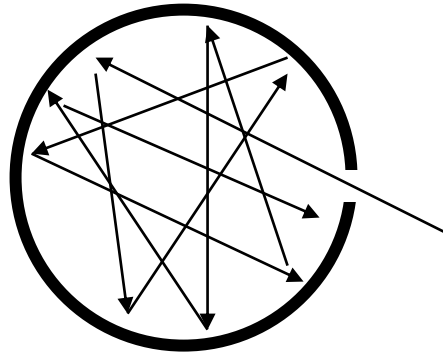
Experiments showed that blackbody radiation depends only on the temperature of the object (*but curiously, not on its composition!*).
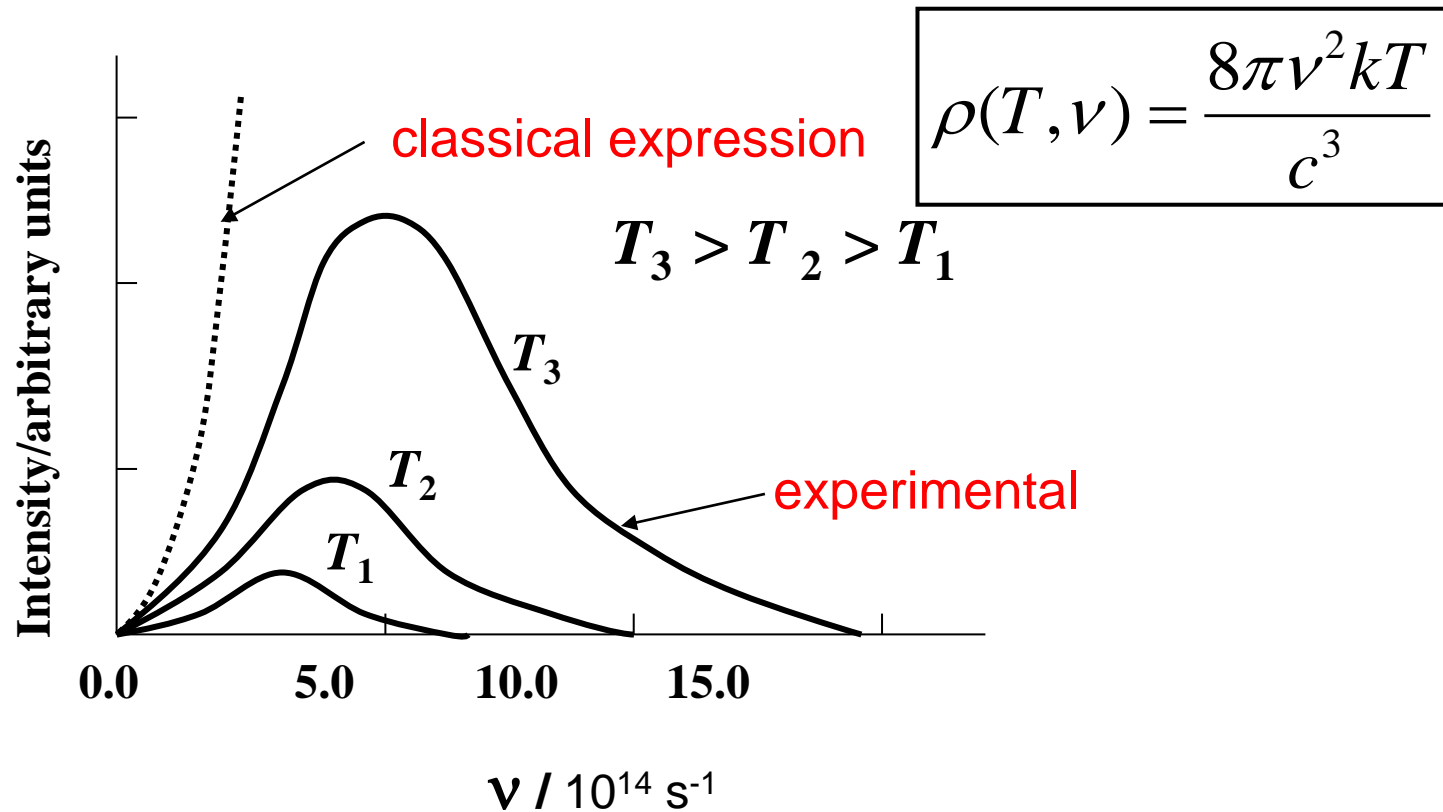
An excellent approximation to a true blackbody radiator is arranged by cutting a small hole in the wall of a hollow cavity. No radiation entering the hole from the outside escapes – it is all absorbed by the walls. The radiation leaking out of the hole is blackbody radiation (also called "**cavity radiation**").
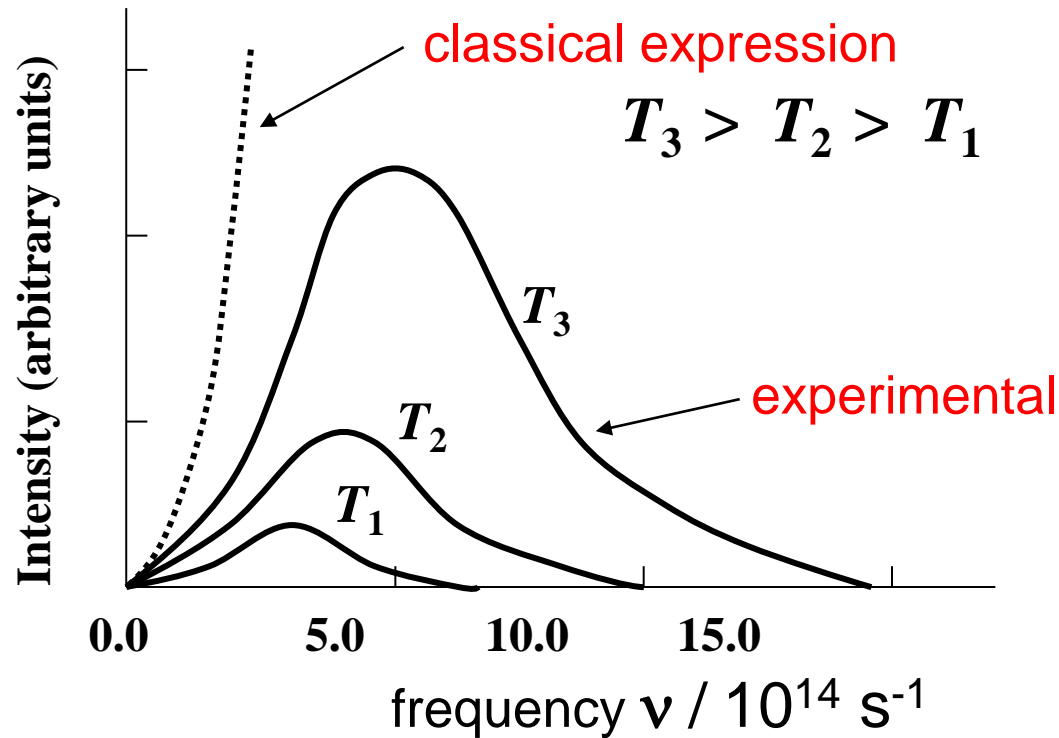
A plot of the intensity of the blackbody radiation as a function of the frequency of the radiation.

Many attempts were made to derive expressions for the blackbody spectrum measured in experiments.

Most resulted in expressions for the intensity that grew without bound (the dashed curve) with increasing frequency.

$$\rho(T, \nu) = \frac{8\pi \nu^2 kT}{c^3}$$

classical expression

$T_3 > T_2 > T_1$

T_3

experimental

T_2

T_1

0.0   5.0   10.0   15.0

ν / 10^{14} s^{-1}

In the classical treatment, radiation emitted by a blackbody was assumed to be due to oscillations of electrons (like electrons in an antenna that give off radiation).

In classical physics, these oscillating systems could have any energy and could radiate any frequency.

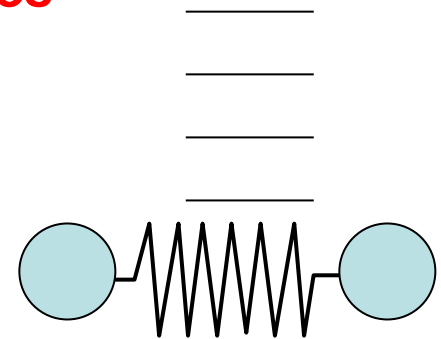# Planck's Interpretation and the Idea of Quantization

In 1900, Max Planck proposed a revolutionary idea:

the energy of the oscillators and the oscillation frequencies could only be integer multiples of certain values

$$E = n\, h\, \nu \qquad n = 0, 1, 2, 3\ldots$$

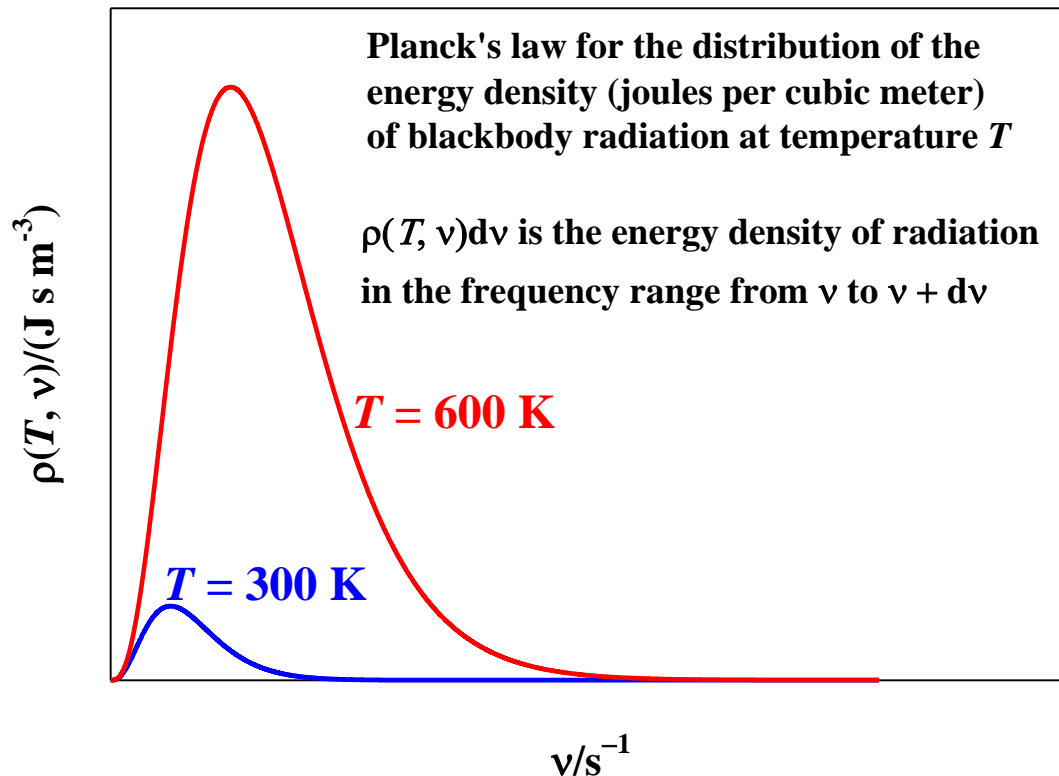h a constant of proportionality

ν radiation frequency

In other words, Planck proposed that the energy of the oscillators was *quantized* and that only certain quantities of light energy could be emitted: $E_1 = h\nu_1,\ E_2 = h\nu_2,\ E_3 = h\nu_3,\ \ldots$

But in classical physics, physical quantities are allowed to take on a *continuous* values. "Quantization" was not initially accepted.

By *assuming* energy quantization, Planck derived expressions that accurately reproduced the measured spectrum of blackbody radiation using the constant **h = 6.626 x 10^{-34} J s**

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

Planck's law for the distribution of the energy density (joules per cubic meter) of blackbody radiation at temperature T

$\rho(T, \nu)d\nu$ is the energy density of radiation in the frequency range from ν to $\nu + d\nu$

$T = 600$ K

$T = 300$ K

$\rho(T, \nu)/(\text{J s m}^{-3})$

ν/s^{-1}

Nobel Prize for the discovery of energy quanta.

What's going on ?

classical (*incorrect* !) spectrum
of thermal radiation

$$\rho(T,\nu)_{\text{classical}} = \frac{8\pi h\nu^2 kT}{c^3}$$

Planck's (*correct* !) spectrum
of thermal radiation

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

Notice:

$$\rho(T,\nu) = \frac{h\nu}{kT} \frac{1}{e^{h\nu/kT} - 1} \rho_{\text{classcial}}(T,\nu)$$

What's going on ?

$$\rho(T,\nu) = \frac{h\nu}{kT} \frac{1}{e^{h\nu/kT} - 1} \rho_{\text{classcial}}(T,\nu)$$

Planck's equation applies the "correction factor" $\dfrac{h\nu}{kT} \dfrac{1}{e^{h\nu/kT} - 1}$

to the classical expression for the thermal radiation spectrum. *Why*? At temperature *T*, using the Boltzmann distribution, the probability of oscillator energy *nhv* is proportional to e$^{-nhv/kT}$ and the average energy of the **quantized** thermal oscillators is

$$< h\nu > \ = \ \sum_{n=0}^{\infty} P_n n h\nu \ = \ \frac{0 \ + \ h\nu e^{-h\nu/kT} \ + \ 2h\nu e^{-2h\nu/kT} \ + \ 3h\nu e^{-3h\nu/kT} \ + \ \cdots}{1 \ + \ e^{-h\nu/kT} \ + \ e^{-2h\nu/kT} \ + \ e^{-3h\nu/kT} + \ \cdots}$$

$$= \ \frac{h\nu}{e^{h\nu/kT} - 1}$$

Applications of Thermal Radiation ?

Important applications covered next week.
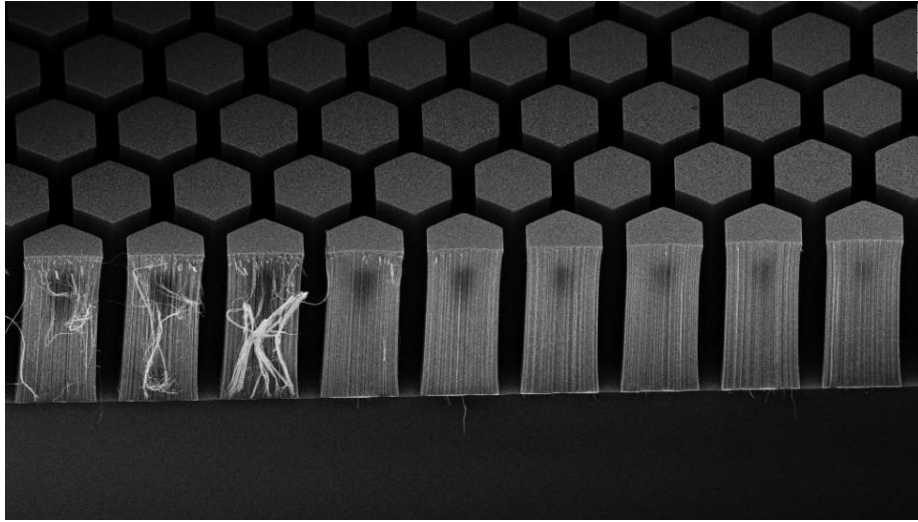
Interesting application: **Vantablack^{TM}** pigment

The darkest black substance ever synthesized.

Absorbs > 99.9 % of incident light.

Constructed from **v**ertically **a**ligned **n**ano**t**ubes.

Vantablack™

a second "violation" of classical physics:

2. Heat Capacity of Monatomic Crystals

In the early 1800s, French scientists Dulong and Petit measured heat capacities at constant volume (the change in energy per degree) for different materials.

$$C_{Vm} = (\partial U_m / \partial T)_V$$

They found $C_{Vm} \approx$ **25 J K^{-1} mol^{-1} for monatomic crystals**, such as lead and other metals. This is easily understood using classical physics: each atom oscillates in three dimensions (x, y, z) and each of these "degrees of freedom" according to the **equipartition theorem** has on average energy equivalent to kT. T is the temperature and k is Boltzmann's constant (1.38066×10^{-23} J K^{-1}).

Then for one mole $U_{Vm} \approx N_{Avogadro} \times 3kT = 3RT$ for the molar energy and $C_{Vm} = [\partial(3RT)/\partial T]_V = 3R = 24.9$ **J K^{-1} mol^{-1}** for the molar heat capacity, in good agreement with Dulong and Petit's experiments.

But …

As technology improved, it became possible to measure heat capacities at very low temperatures (approaching absolute zero, $T = 0\ \mathbf{K}$). For some reason, unknown at the time, the heat capacities of cold monatomic crystals dropped well below the predicted $3R$ value. Something was literally:

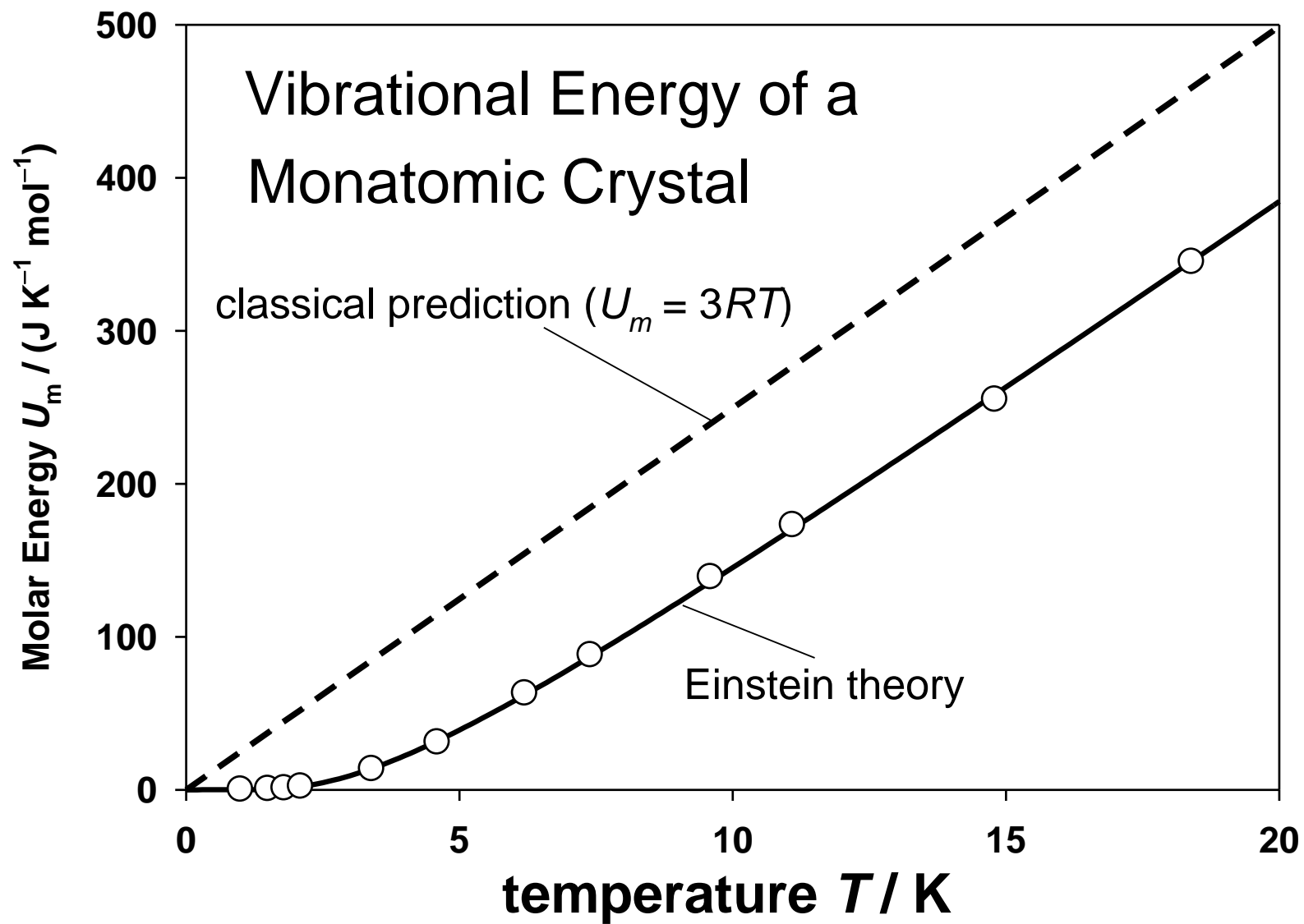*freezing out atomic vibrations at low temperatures*

Why ? …

Einstein's Solution: *Quantized Atomic Vibrations*

Following Planck's success in accounting for blackbody radiation by allowing for only discrete "chunks" of radiation energy, Einstein provided a solution to the heat capacity problem by assuming that the allowed energies of atomic vibrations are not continuous, but can only have discrete *quantized* values:

$$0,\ h\nu,\ 2h\nu,\ 3h\nu,\ 4h\nu,\ \ldots$$

h is Planck's constant, ν is the fundamental vibrational frequency.

Vibrational Energy of a Monatomic Crystal

classical prediction ($U_m = 3RT$)

Einstein theory

Molar Energy U_m / (J K^{-1} mol^{-1})

temperature T / K
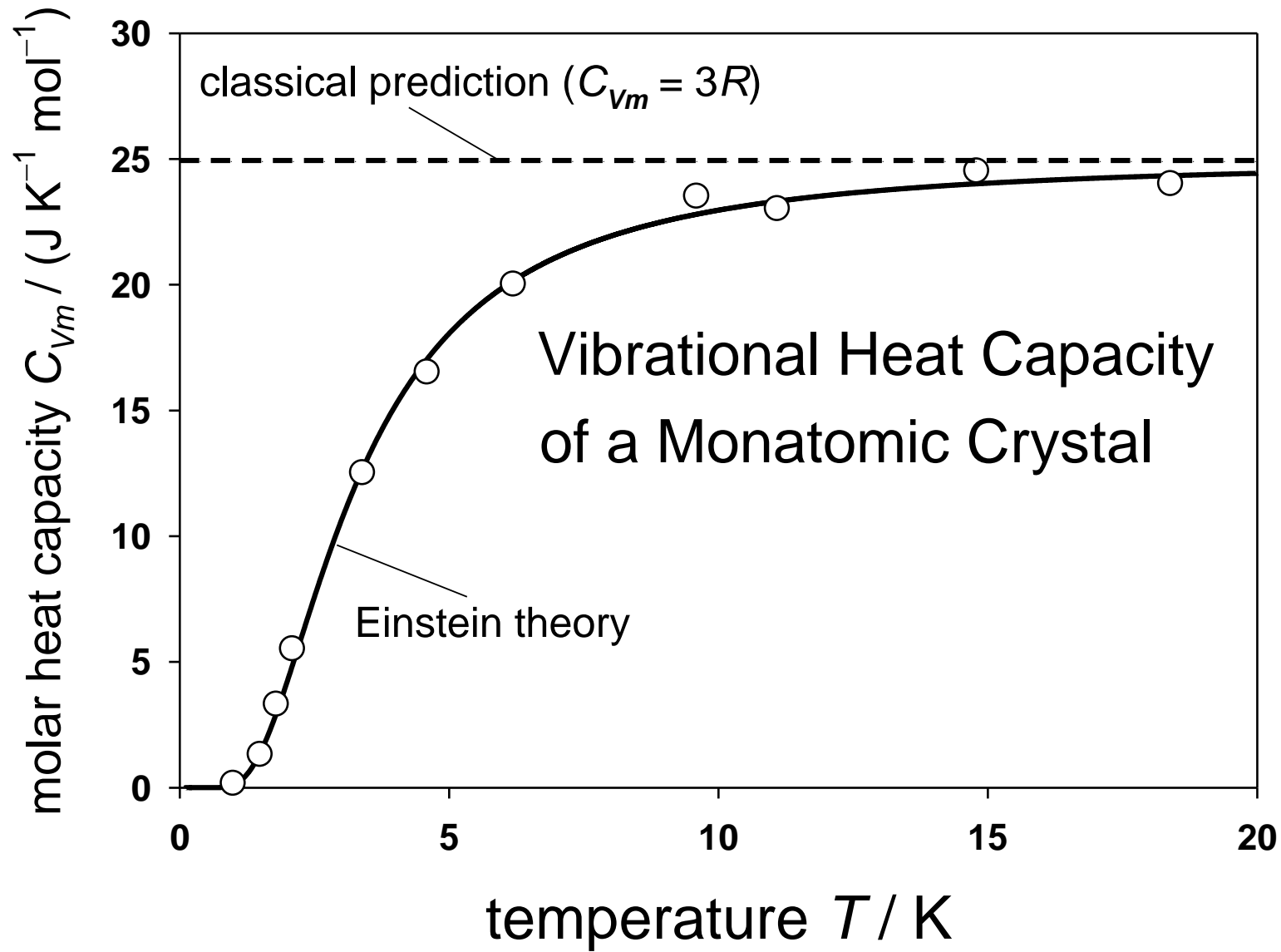
Einstein's calculations:

According to the recently discovered ***Boltzmann distribution law***, Einstein reasoned the probability of finding an atom oscillating with energy $nh\nu$ is proportional to $\mathrm{e}^{-nh\nu/kT}$ with $n = 0, 1, 2, 3, \ldots$

So the average vibrational energy per atom (in three dimensions) is

$$U_{\mathrm{m}}(T) = 3\,\frac{0 + h\nu\mathrm{e}^{-h\nu/kT} + 2h\nu\mathrm{e}^{-2h\nu/kT} + 3h\nu\mathrm{e}^{-3h\nu/kT} + \cdots}{1 + \mathrm{e}^{-h\nu/kT} + \mathrm{e}^{-2h\nu/kT} + \mathrm{e}^{-3h\nu/kT} + \cdots}$$

After some algebra, the average vibrational energy per mole is

$$U_{\mathrm{m}}(T) = 3RT\,\frac{h\nu}{kT}\frac{1}{\mathrm{e}^{h\nu/kT} - 1}$$

Limits? As an informative exercise, use Einstein's equation to show:

  1. as $T \to 0$ ($h\nu \gg kT$), $U_m \to 0$ ("**new**" **quantum behavior**)

  2. as $T \to \infty$ ($h\nu \ll kT$), $U_m \to 3RT$ (**classical behavior**)

Einstein's Expression for the Molar Heat Capacity of a Monatomic Crystal

Taking the temperature derivative of U_m gives

$$C_{Vm} = \frac{dU_m(T)}{dT} = 3R\left(\frac{h\nu}{kT}\right)^2 \left(\frac{e^{h\nu/2kT}}{e^{h\nu/kT}-1}\right)^2$$

with: $C_{Vm} \rightarrow 0$ as $T \rightarrow 0$ ($h\nu \gg kT$, all vibrations *frozen* out)

$C_{Vm} \rightarrow 3R$ as $T \rightarrow \infty$ ($h\nu \ll kT$, the classical limit)

Good agreement with experiment.

And the value of h from the heat capacities agreed with the value from the analysis of blackbody radiation !

closely related ….

3. <u>Heat Capacity of Ideal Diatomic Gases</u>

For the heat capacities of diatomic gases, such as O_2 and N_2 in air, **<u>classical mechanics predicts</u>:**

$$C_{Vm} = (\partial U_m / \partial T)_V$$

$$= 7R/2$$

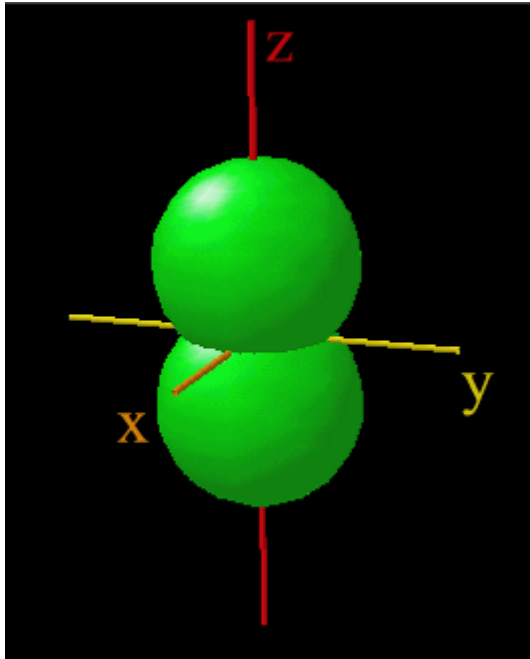$$= 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

But **<u>experimentalists measure</u>:**

$$C_{Vm} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1} \approx 5R/2$$

<u>*Why*</u> ? Just as quantum vibrations of atoms are "frozen out" for cold crystals, diatomic molecules are not actively vibrating, except at very high temperatures.

Equipartition Theory: each energy mode contributes

(classical) $RT/2$ to the molar energy for a **diatomic ideal gas** (*from Chem 231/232*):

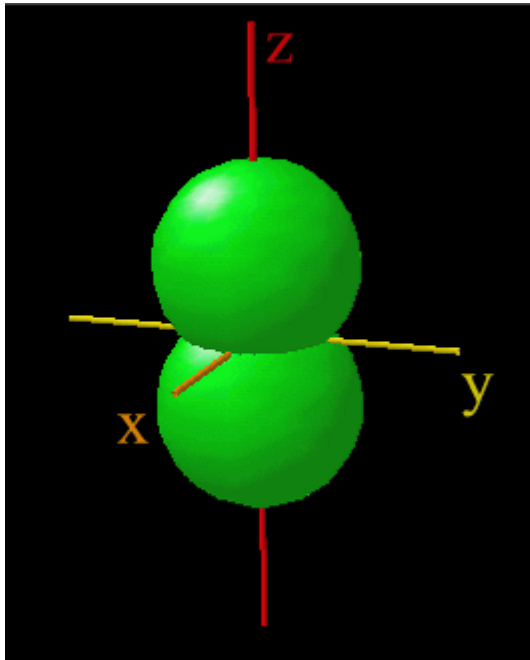|	
x-velocity kinetic energy	$RT/2$
y-velocity kinetic energy	$RT/2$
z-velocity kinetic energy	$RT/2$
x-axis rotation	$RT/2$
y-axis rotation	$RT/2$
z-axis vibration kinetic energy	$RT/2$
z-axis vibration potential energy	$RT/2$

_____

Total energy per mole: $U_m = 7RT/2$

heat capacity prediction $C_{Vm} = (\partial U_m / \partial T)_V$

$$= d(7RT/2)/dT$$

$$= 7R/2$$

$7R/2$ is the classical heat capacity prediction. But experiments give $C_{Vm} = 5R/2$.
An R is missing! Why?

Equipartition Theory: each energy mode contributes **(quantum)** $RT/2$ to the molar energy for a **diatomic ideal gas** (*from Chem 231/232*):

|	
x-velocity kinetic energy	$RT/2$
y-velocity kinetic energy	$RT/2$
z-velocity kinetic energy	$RT/2$
x-axis rotation	$RT/2$
y-axis rotation	$RT/2$
~~z-axis vibration kinetic energy~~	~~$RT/2$~~ **frozen**
~~z-axis vibration potential energy~~	~~$RT/2$~~ **out**

Total energy per mole: $U_m = 5RT/2$

heat capacity prediction $C_{Vm} = (\partial U_m / \partial T)_V$

(no vibration contribution) $= d(5RT/2)/dT$

$= 5R/2$

Quantum mechanical vibrational energy levels are too high in energy to be significantly occupied, except at very high temperatures.

4. The Photoelectric Effect

Another phenomena of historic interest that "deviated" from classical physics was the photoelectric effect.

Photoelectric effect: The ejection of electrons from the surface of a metal by radiation.

light

e⁻

kinetic energy of emitted electrons can be measured

Metal surface
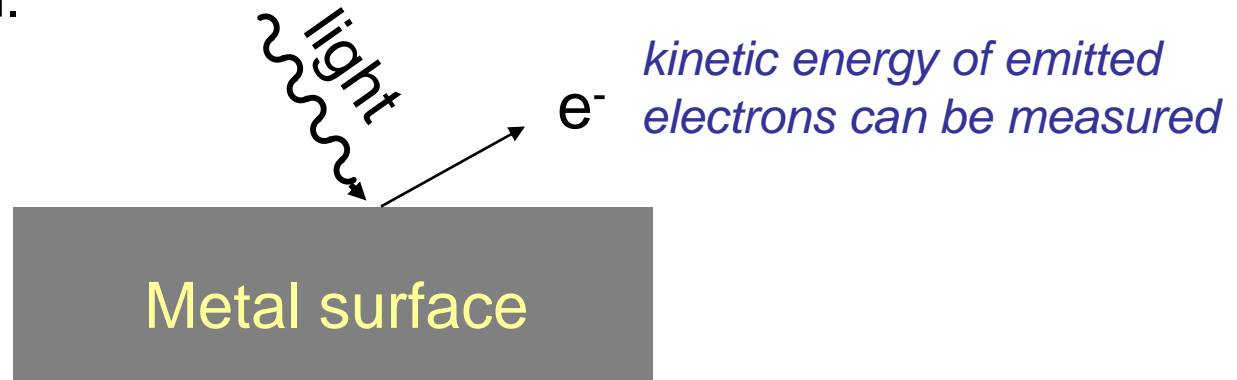
The classical picture of light is an oscillating electromagnetic wave. Electrons at the surface oscillate with the changing electric field so violently that they get knocked out or emitted.

This classical picture predicts the kinetic energy of the electrons should increase as the **amplitude** of the radiation (intensity) increases.

The Photoelectric Effect

light

e⁻

Metal surface
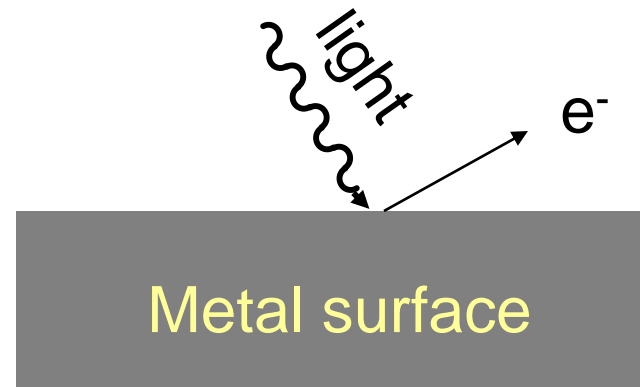
Curious Experimental Observations:

- The kinetic energy of the ejected electrons increases with the **frequency** of the light, *not its intensity*.

- No matter how intense the light of a given frequency, the energy of the ejected electrons remains the same.

- Increasing the light intensity increases the number of electrons ejected, but not their kinetic energy.

- For each metal, no electrons are ejected below a threshold frequency of the light specific to that metal.

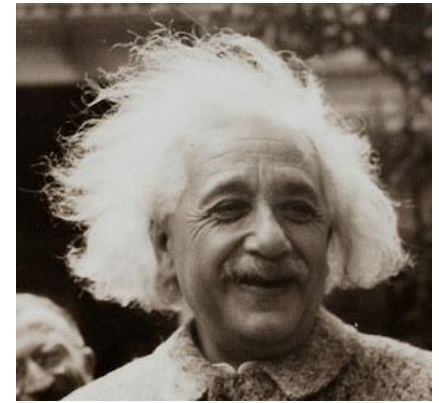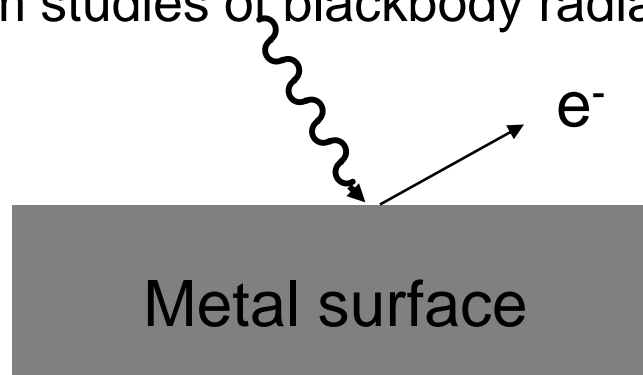# Einstein's Interpretation of the Photoelectric Effect

Einstein made a major conceptual extension to Planck's concept of quantization, that *radiation exists as small packets of energy,* now called *photons*.

$$E = h\nu = hc / \lambda$$

The kinetic energy of the ejected electrons is the energy of the incident photon minus the potential energy (the work function ϕ) holding the electron in the metal.

Nobel Prize for the explanation of the photoelectric effect.

$$\tfrac{1}{2}m\mathbf{v}^2 = h\nu - \phi$$

The slope of the electron kinetic energy plotted against frequency was in good agreement with Planck's h value from studies of blackbody radiation and heat capacities!

e⁻

Metal surface

The same constant h determined from completely different experiments!

Measurement of the Photovoltaic Effect

To measure the maximum kinetic energy of emitted photoelectrons, apply a negative potential to stop all photoelectrons reaching the collector plate.

incident radiation

emitter plate   +   **electrons**   **collector plate**   −

evacuated quartz tube (*why quartz* ?)

volt meter

variable dc voltage

amp meter
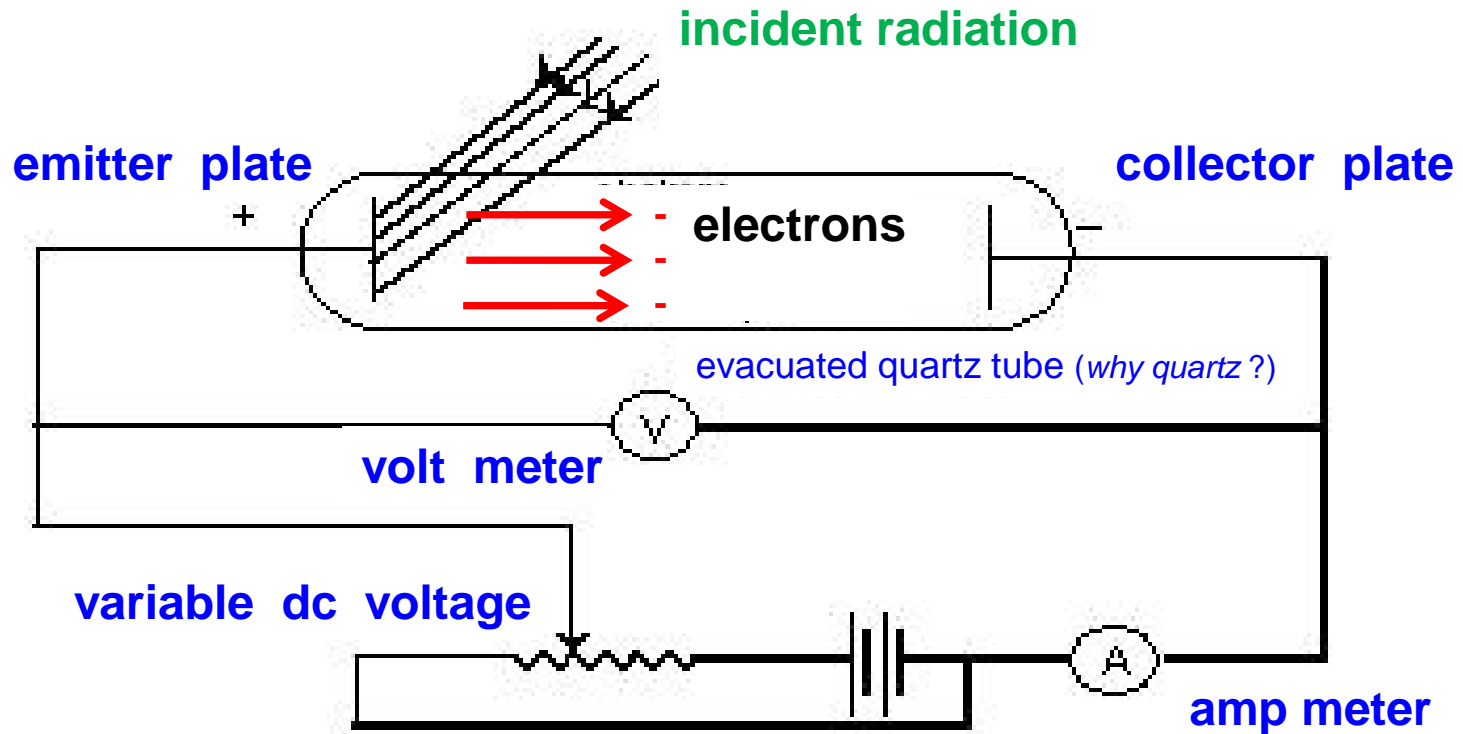
Apply a negative "stopping" potential to the collector plate to
Measure the maximum kinetic energy of the emitted electrons.

Photoelectron Data for Sodium Metal

Exercise : show that the slope of the plot is *h* (Planck constant)

Maximum photoelectron kinetic energy in eV

Light below a frequency of

4.39 x 10^{14} Hz

or wavelength longer than 683 nm would not eject electrons.

The fact that this plot was not dependent upon the intensity of the incident light implied that the interaction was like a particle which gave all its energy to the electron and ejected it with that energy minus that which it took to escape the surface.

Frequency, Hz x 10^{14}

Data from Millikan, 1916

Important application of the photoelectric effect (one of many):

Photomultiplier Tubes

Ultrasensitive radiation detectors. Can detect single photons.
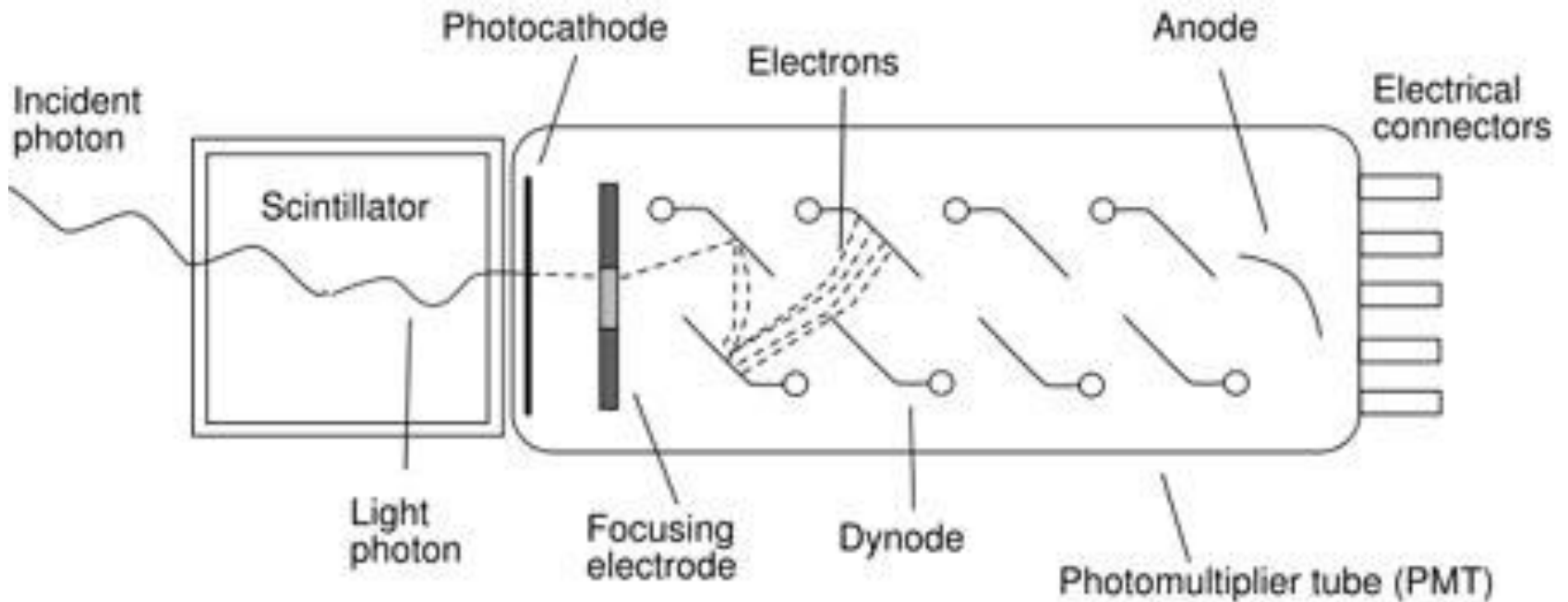
Some energy magnitudes and units

Using Einstein's relation $E = h\nu$ between the energy of a photon and its frequency and the relation $c = \lambda\nu$ between the frequency, wavelength and speed of light (c = 2.99792458 x 10^8 m s^{-1}), the energy of one photon of yellow light (600 nm) is:

$$E = h\nu = hc/\lambda = 3 \times 10^{-19} \text{ J}$$

Electron Volt When dealing with energies of individual photons, units of electron volts (eV) are commonly used (the energy required to drop one electron through one volt or to raise one proton through one volt):
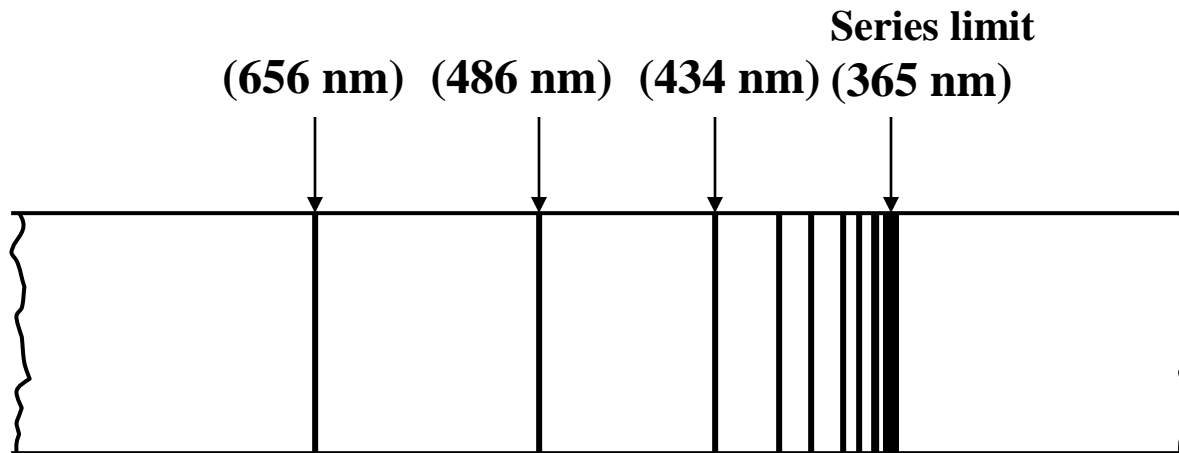
$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

A photon of yellow light has an energy of about 2 eV.

An O_2 bond energy is about 498 kJ/mol, which is about 5.2 eV.

5. Discrete Emission Spectra of the Hydrogen Atom (*and other atoms too*)

Discrete **line spectra** of atoms also suggests energy quantization.

Series limit

(656 nm) **(486 nm)** **(434 nm)** **(365 nm)**

Balmer, Rydberg and others *empirically* derived a formula for the hydrogen line spectra:

$$\nu = \text{constant} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

n_1, n_2 are integers with $n_2 > n_1$ and the **Rydberg constant** is 3.28803×10^{15} s^{-1}

Hydrogen spectra controlled by two integers - further evidence for some kind of *quantization*.

Bohr Model of the Hydrogen Atom

The classical picture of an electron and proton cannot explain the discrete ("line") emission spectra.

Bohr came *close*. He *assumed* that the angular momentum of the electrons is quantized with *allowed* values $\mu v r = n h/2\pi$

$$h/2\pi, \ 2(h/2\pi), \ 3(h/2\pi), \ 4(h/2\pi), ...$$

The centrifugal force on the rotating electron is balanced by the attractive Coulombic force

$$\mu v^2/r \ = \ e^2/(4\pi\varepsilon_0)r^2 \quad \text{or} \ \ \mu^2 v^2 r^2 \ = \ (nh/2\pi)^2 \ = \ [\mu e^2/(4\pi\varepsilon_0)]r$$

then *r* is quantized too!

$\mu = m_e m_p/(m_e + m_p) \approx m_e$ is the reduced mass of the proton and electron, v is the electron velocity, r is the distance between the proton and electron, and ε_0 is the vacuum permittivity.

Angular momentum. *What is it?*

Linear momentum for the motion of a particle in one direction is the product mv of the particle mass m and the particle velocity v.

A particle rotating at a distance r from a fixed center moves through the distance $2\pi r$ (one circumference) per revolution at the speed $r\omega$ where the ω is the **angular velocity** defined as the number of radians per second (2π radians per revolution).   So $v = \omega r$.

The kinetic energy of a particle is $\frac{1}{2}mv^2 = \frac{1}{2}mr^2\omega^2$ suggesting the analogies:

$m \leftrightarrow I$ between the mass m and moment of inertia $I = mr^2$

$v \leftrightarrow \omega$ between linear and angular velocities

$mv \leftrightarrow I\omega$ between linear and angular momentum.

Angular momentum $= I\omega = mr^2 v/r = mvr$

Assuming quantized angular momentum, the radii are $r = n^2 a_0$ where a_0 is the radius of a ground-state hydrogen atom ($n = 1$):

Bohr radius: $\quad a_0 = \varepsilon_0 h^2 / \pi \mu e^2 = 52.9177 \times 10^{-12}$ m

Adding the kinetic energy $\mu v^2/2$ and the potential energy $-e^2/(4\pi\varepsilon_0)r$ from Coulomb's law, Bohr derived the expression $E_n = -\mu e^4/(8n^2 h^2 \varepsilon_0{}^2)$ for the quantized energies of a hydrogen atom.

Using the energy change $\Delta E = E_{n2} - E_{n1} = h\nu$ for a hydrogen emission line for a transition from n_2 to n_1 gave the frequencies:

$$\nu = \frac{\mu e^4}{8\varepsilon_o^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Except for the assumption of angular momentum quantization, the Rydberg equation was derived with classical mechanics.

μ = reduced mass of electron and proton = $m_e m_p / (m_e + m_p) \approx m_e$

m_e = electron mass   (9.10939 x 10^{-31} kg)

m_p = proton mass   (1.67262 x 10^{-27} kg)

e = elementary charge   (1.602177 x 10^{-19} C)

ε_0 = vacuum permittivity   (8.85419 x 10^{-12} J C^2 m^{-1})

h = Planck's constant   (6.62608 x 10^{-34} J s)

Using $c = \lambda \nu$ and expressing frequencies in wavenumbers ($\lambda^{-1} = \nu / c$):

Bohr predicted (in amazing agreement with experiment):

$\nu / c = (109{,}677 \text{ cm}^{-1})(1/n_1^2 - 1/n_2^2)$ *Hydrogen Emission Spectra*

Experimentalists measured: **(n_2 to n_1)**

$\nu / c = (109{,}677.576 + \text{ or} - 0.012 \text{ cm}^{-1})(1/n_1^2 - 1/n_2^2)$

Lyman series: $n_1 = 1, n_2 = 2, 3, 4, \dots$ (ultraviolet)

Balmer series: $n_1 = 2, n_2 = 3, 4, 5, \dots$ (visible)

Paschen series: $n_1 = 3, n_2 = 4, 5, 6, \dots$ (infrared)

Pfund series: $n_1 = 4, n_2 = 5, 6, 7, \dots$ (infrared)

de Broglie's Wave Nature of Matter

A <u>conceptual break through</u> came from de Broglie in 1923.

By then the dual wave-particle nature of light was accepted by most leading physicists.

de Broglie extended and ***quantified*** the wave-particle duality of light to all particles (electrons, protons, baseballs).

Using special relativity, Einstein had derived an expression for the momentum of a photon (even though it has no mass). Using a similar line of reasoning, de Broglie argued that the ***wavelength λ of any particle is related to its momentum $p = m v$*** as follows:

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

h **is Planck's constant, *again!***

For photons, which travel at the speed of light (c), combining

$$E = h\nu = hc/\lambda$$

and

$$E = mc^2 \qquad \text{(from the theory of relativity)}$$

gives

$$\lambda = h/mc$$

de Broglie extension to **particles** of mass m moving at velocity $\mathbf{v}$:

$$\lambda = h/m\mathbf{v} = h/p$$

And de Broglie's concept of the wave nature of particles explained Bohr's assumption that the angular momentum of electrons in H atoms are quantized! For an electron in a stable orbit around a proton, the orbit circumference is an integer multiple of the electron wavelength ($2\pi r = n\lambda$) which gives quantized angular momentum:

$$m\mathbf{v}r = nh/2\pi \qquad \text{(Bohr's assumption)}$$

In 1925, experimental verification of the particle wave hypothesis came with electron diffraction experiments.
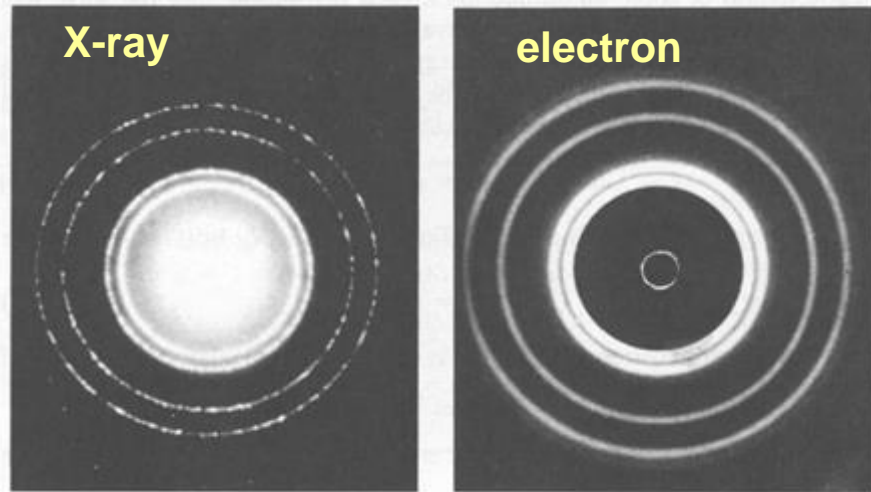
X-ray and electron diffraction patterns through aluminum foil

Louis de Broglie, Nobel Prize for the discovery of the wave nature of electrons.

Today, the wave property of matter is used routinely:

- electron microscopes (electron microscopes have shorter wavelengths and higher resolution than optical microscopes)
- neutron diffraction

Wave-particle duality of matter is significant only for very small particle masses.

$$\lambda = \frac{h}{m\mathrm{v}} = \frac{h}{p}$$

Particle	Mass (kg)	Speed (m/s)	Wavelength (1 pm = 0.001 nm)
Electron accelerated through 100 V	9.11×10^{-31}	5.9×10^{6}	**120 pm** **(atomic and molecular distances)**
Alpha particle ejected from radium	6.68×10^{-27}	1.5×10^{7}	6.6×10^{-3} pm (smaller than an atom)
Bullet	1.9×10^{-3}	3.2×10^{2}	1.1×10^{-21} pm (much smaller than a nucleus)

For macroscopic bodies, de Broglie wavelengths are completely undetectable and of no practical consequence.
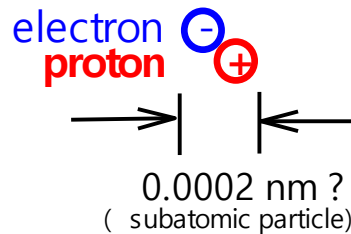
Recall the important question about the <u>existence of atoms:</u>

Why doesn't the electron spiral inwards to merge with the proton, forming a **subatomic particle** (diameter << 0.10 nm for H atoms)?
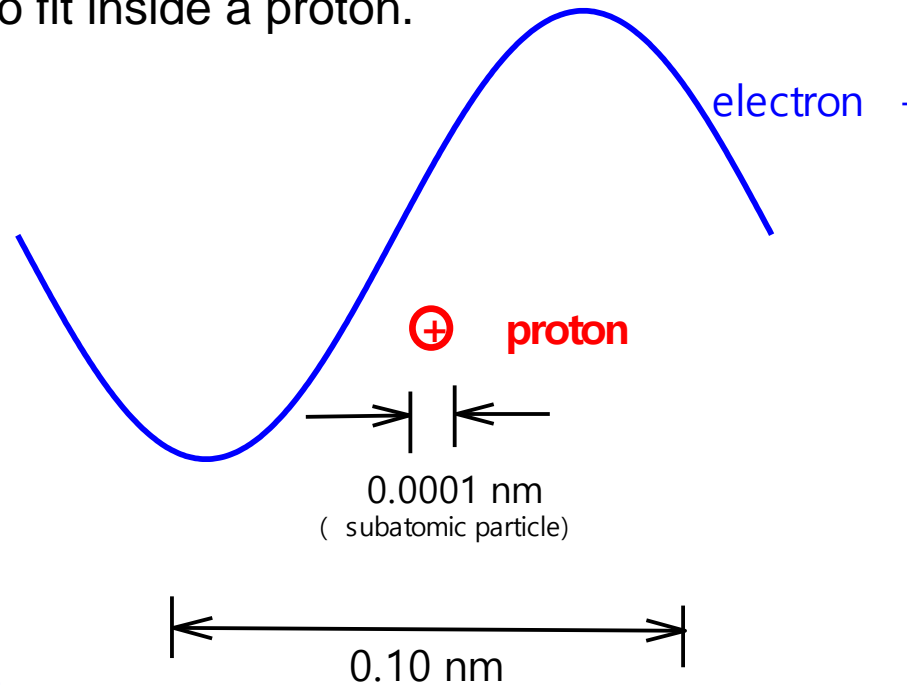
<u>Hydrogen Atom</u>

electron and a proton

positive and negative charges attract:

electron ⊖
proton ⊕

0.0002 nm ?
(subatomic particle)

Answer: electrons are <u>waves</u> !

At typical energies ($\approx$ 10 eV), the wavelength of an electron is $\approx$ 0.1 nm, much too large* to fit inside a proton.

electron   -

$\oplus$ **proton**

0.0001 nm
(subatomic particle)

0.10 nm

Huge **Significance:**

- formation of atomic (1s, 2s, 2p, …) and molecular orbitals as "standing" waves

- standing (resonance) waves have fixed energy $\rightarrow$ quantization of energy

- existence of atoms and molecules **(*and all of chemistry* !)**

*At <u>very high</u> energies (millions of eV), electron wavelengths are much smaller, allowing electrons and protons to merge, as in the formation of neutron stars.

Wave-Particle Duality

Wave-particle duality refers to the fact that both light and matter can exhibit particle-like behavior or wave-like behavior depending on how we observe them.

In other words, their behavior depends on the nature of the experiment.

• photons can behave like particles in a photo-electric experiment

• electrons and other particles can exhibit a wave-like diffraction patterns
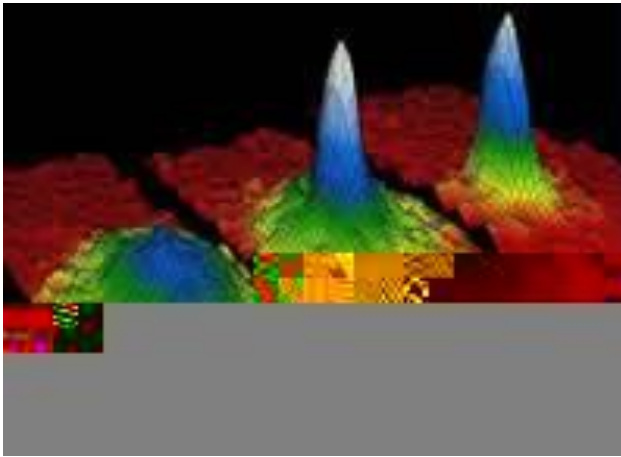
The density of an atomic cloud as the temperature is decreased (left to right): wave-like behavior

Cooling Technology

Atoms are first cooled by lasers, then confined by a magnetic trap.

Evaporative cooling is the last step.

Atoms can all be described by a single wave function!

2001 Nobel Prize in Physics

Eric A. Cornell
JILA and National Institute of Standards and Technology (NIST), Boulder, Colorado, USA,

Wolfgang Ketterle
Massachusetts Institute of Technology (MIT), Cambridge, Massachusetts, USA, and

Carl E. Wieman
JILA and University of Colorado, Boulder, Colorado, USA,

"for the achievement of **Bose-Einstein condensation** in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates".
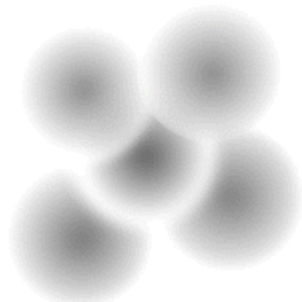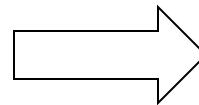
Bose   Einstein

Cooling rubidium atoms to less than 170 billionths of a degree above absolute zero caused the individual atoms to condense into a "superatom" behaving as a single entity

a few thousand atoms

Some very cold atoms

Some atoms in a BEC condensate

Heisenberg Uncertainty Principle
mid 1920s

The wave-particle duality of both light and matter leads to some very awkward results.

Consider the measurement of the position of an electron.

If we want to locate the electron within a distance Δx, we must use spatial **resolution** less than Δx.

One way to achieve this is to use light of wavelength $\lambda \approx \Delta x$.

For us to 'see' the electron, the photon must interact with the electron.

But the photon has a momentum associated with it. $\quad p = \dfrac{h}{\lambda}$

Thus, the very act of observing the electron leads to a change in its momentum.

Heisenberg Uncertainty Principle

Classical mechanics: no limitations on the accuracy of measurements
of position, velocity, momentum, … of particles

But wait !   From quantum mechanics, *particles are actually waves* !

For wave motion (from Fourier integral methods):

$$\Delta x \, \Delta \frac{1}{\lambda} \;\geq\; \frac{1}{4\pi}$$

Example:

A Monochromatic Wave (one fixed wavelength λ) Moving at Velocity v

$$\psi(x,t) \;=\; A\sin\left[\frac{2\pi}{\lambda}\left(x \,-\, vt\right)\right]$$

$$\Delta \frac{1}{\lambda} \;=\; 0 \qquad \text{so} \qquad \Delta x \;=\; \infty \qquad \textit{It's everywhere} !$$

Heisenberg Uncertainty Principle

$$\Delta x \, \Delta \frac{1}{\lambda} \;\geq\; \frac{1}{4\pi}$$

Wave Packet: A Superposition of *N* Different Waves

$$\psi(x,t) \;=\; \sum_{i=1}^{N} A_i \sin\left[\frac{2\pi}{\lambda_i}(x \,-\, \mathrm{v}t) \right]$$

As the number N of different wavelengths increases, $\Delta(1/\lambda)$ increases, so Δx decreases, causing the wave packet to be more localized in space, behaving more like a particle.

Heisenberg Uncertainty Principle

$$\Delta x \, \Delta \frac{1}{\lambda} \;\geq\; \frac{1}{4\pi}$$

Delta Function (superposition of ∞ different waves)

$$\psi(x,t) \;=\; \sum_{i=1}^{\infty} A_i \sin\left[\frac{2\pi}{\lambda_i}\left(x \;-\; vt\right)\right]$$

In the limit of an infinite number of superimposed waves, $\Delta(1/\lambda) \;=\; \infty$ and $\Delta x \;=\; 0$, so the "particle" is exactly located.

Heisenberg Uncertainty Principle

$$\Delta x \, \Delta \frac{1}{\lambda} \;\; \geq \;\; \frac{1}{4\pi}$$

wave velocity = frequency × wavelength

$$\mathrm{v} \;\; = \;\; \nu \; \lambda$$

divide and multiply by v:

$$\Delta \frac{x}{\mathrm{v}} \, \Delta \frac{\mathrm{v}}{\lambda} \;\; \geq \;\; \frac{1}{4\pi} \qquad \longrightarrow \qquad \Delta t \, \Delta \nu \;\; \geq \;\; \frac{1}{4\pi}$$

Application to spectroscopy:

Transitions involving long-lived states (large Δt) absorb or emit nearly monochromatic radiation.

Short-lived states produce broader ranges of frequencies.

Heisenberg Uncertainty Principle

$$\Delta x \, \Delta \frac{1}{\lambda} \;\geq\; \frac{1}{4\pi}$$

Multiply by Planck constant h:

$$\Delta x \, \Delta \frac{h}{\lambda} \;\geq\; \frac{h}{4\pi}$$

Recall that h/λ is the momentum p (the de Broglie relation):

$$\Delta x \, \Delta p \;\geq\; \frac{h}{4\pi}$$

Usually written as:

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

"h-bar" is the Planck constant divided by 2π :

$$\hbar \;\equiv\; \frac{h}{2\pi}$$

Developing this idea more fully, Werner Heisenberg showed that it is not possible to simultaneously determine the **exact** position x and the **exact** velocity v of a particle at the same time.

The smaller the uncertainty Δx in the position of a particle, the larger the uncertainty in the particle's momentum $\Delta p,$ and *vice versa.*

$$\Delta x \, \Delta(m v) \geq \frac{\hbar}{2}$$

Heisenberg Uncertainty Principle

$$\hbar = \frac{h}{2\pi}$$

The uncertainty principle is incompatible with the deterministic classical picture because we cannot specify exactly a particle's position and momentum simultaneously. We can only talk about *probabilities*.

But the uncertainty principle is important only on *microscopic scales*.

h **= 6.626 x 10^{-34} J s**   (*small!*)

e.g. The uncertainty in the position of a baseball (145 g) thrown at 90 mph (40 m/s) if we measure the momentum ($p = m\text{v}$) to a millionth of 1.0% (9 x 10^{-8} mph):

$$\Delta x \Delta p \geq \frac{\hbar}{2} = 5x10^{-35}$$
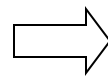
Δp **= 5.6 x10^{-8} kg m/s**

Δx **= 9.4 x10^{-28} m**

(*negligible, less than the radius of atomic nuclei*)

e.g. The uncertainty in the momentum if we locate an electron within an atom so that the uncertainty in its position is 50 pm. (Bohr radius)
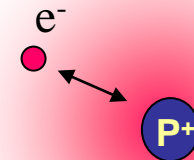
If Δx = 50 x10^{-12} m

Then Δp = $m\Delta v$ = 1.3 x10^{-23} kg m/s $\Longrightarrow$ **Δv = 1 x 10^7 m/s**

e$^-$

P$^+$

Relatively large!

Historical Development of Quantum Mechanics

The stage was set for the development of a new theory to describe the microscopic world of electrons and nuclei.

- classical mechanics combined with ideas of quantization can reproduce experimental observations.

- quantization of energy states with Planck's constant

- wave-particle duality of light and matter

- uncertainty principle starts to hint at probabilities (not classical determinism)

- Boltzmann's law is used to calculate the probabilities that atoms and molecules are in allowed energy states

Modern Physics:

- theory of relativity
- quantum mechanics

Theory of Relativity :   Developed by Einstein in 1905, extended classical mechanics to high velocities and astronomical distances.

Quantum Mechanics :   developed over decades by many scientists. Deals with the microscopic at the level of atoms, electrons and smaller.

Quantum Mechanics has had a profound effect on our understanding of chemistry. For example, covalent bonds cannot be explained by classical physics. There is a sub-discipline of chemistry and quantum mechanics called 'quantum chemistry'.

<u>Quantum Mechanics</u>

Modern quantum mechanics was "discovered" in 1925.

In 1925, during Christmas holidays,
Schrödinger developed the Wave Equation
of quantum mechanics, starting from
de Broglie's idea that particles are waves

Schrödinger's formulation of quantum mechanics,
known as ***Wave Mechanics,*** replaced the "old"
quantum mechanics developed by Bohr.

1933 Nobel Prize

In quantum chemistry, Schrödinger's formulation of quantum mechanics is most frequently used. In other applications, especially nuclear physics, Heisenberg's and other formulations are used.

There are other notable developments of quantum mechanics:

1925 – Heisenberg's Matrix Quantum Mechanics (1932 Nobel Prize)

1926 – Schrödinger showed that Matrix and Wave Mechanics are equivalent

Schrödinger's and Heisenberg's treatments of quantum mechanics do not include Einstein's theory of relativity.

1929 – Dirac – *Relativistic Quantum Mechanics* **(1933 Nobel Prize)**

Complicated, and not widely used in chemistry. Includes antimatter. **Spin** is introduced as a natural variable, just like time or position, but nothing is spinning!

Spin is included empirically in quantum chemistry.

1941 – Feynman (1965 Nobel Prize) – *Path Integral Formulation of Quantum Mechanics*

"*I think it's safe to say that nobody really understands quantum mechanics.*" Richard Feynman, 1965 Nobel Physics Prize for research on quantum electrodynamics.
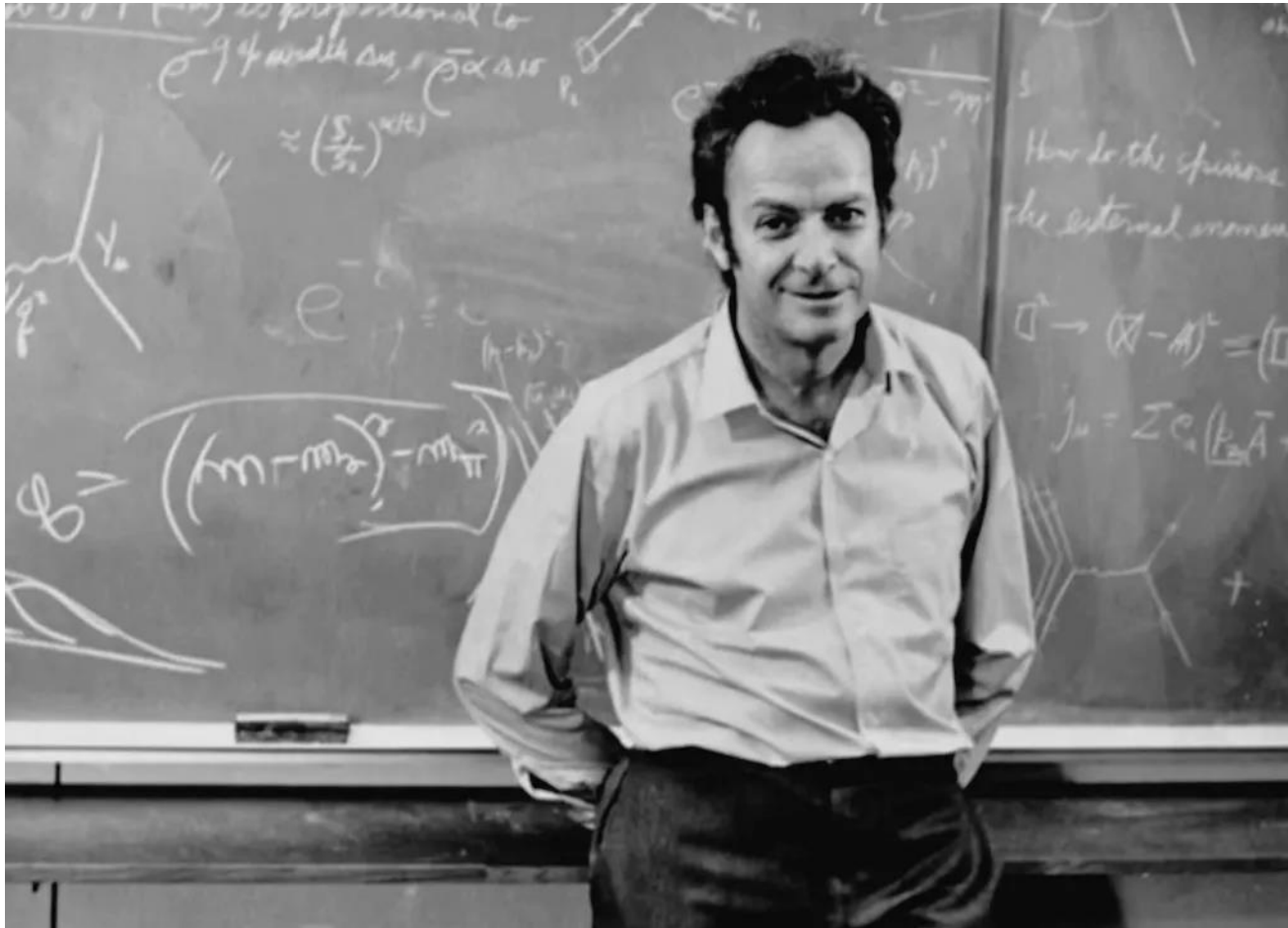
1. Introduction – Why is Quantum Mechanics Important for Understanding Chemistry?

Important topics and terminology:

thermal radiation (*aka* blackbody radiation, *aka* cavity radiation)

quantization	Planck's radiation law	Planck constant h
h bar ($h/2\pi$)	Boltzmann distribution law	$P_i \propto \exp(-E_i/kT)$
crystal vibrations	low-temperature heat capacities	photoelectric effect
Bohr model of the H atom	linear momentum	angular momentum
Bohr radius a_0	continuous spectra	line spectra
Rydberg constant	de Broglie wavelength h/p	de Broglie relation
electron diffraction	wave/particle duality	

Heisenberg uncertainty principle