Chemical Bonding

CHEM 6277-10

Lecture 1

Introduction to Quantum Mechanics

Lecturer: Hanning Chen, Ph.D.

08/29/2017

Who am I ?

Name: Hanning Chen

Title: Assistant Professor of Chemistry

Ph.D., University of Utah
Postdoctoral Fellow, Northwestern University

Research Interests: Theoretical and Computational Chemistry

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Research Group Website: http://www.chenlabgwu.net

Syllabus

Course Name: Chemical Bonding

Course Number: CHEM 6277

Course Credits: 3, graduate level

one of the three "**core**" courses in **physical chemistry** division

Course Textbook: *Quantum Chemistry, 7th Edition*, Ira N. Levine, ISBN 978-0321803450

Lecture Room: Room 311, 1957 E Street

Lecture Schedule: 3:45 PM-5:00 PM, Tuesdays and Thursdays

From **08/29/2017** to **12/05/2017** except for university holidays

10/17/2017: midterm examination

12/13/2017: final examination

Course Objectives

- The **probabilistic** and **delocalization** nature of quantum mechanics.
- Electrons are **indistinguishable** in many-body systems.
- Proper expression of **anti-symmetric** electron wave functions.
- Various ways to solve the time-independent **Schrödinger equation**.
- Perturbation methods to treat **electron correlation** and **excitation**.
- Justify **physical properties** from electronic structure calculations.
- **Hands-on experiences** on popular quantum chemistry software.

Course Organization

a total of **26** lectures, each of which is **75**-minute long

10 min — **Quiz:** assess your understanding of the **immediate past lecture**

55 min — **Lecture**

10 min — **Homework Review:** answer your questions on the **most recently graded assignments**

Grading

Maximum Point: **100**

(a total of 25)	In-class quiz: **25**	1 point/quiz
(a total of 25)	Homework: **25**	1 point/assignment
(Lecture 1 to 13)	Midterm exam: **25**	
(Lecture 14 to 26)	Final exam: **25**	

Final letter grades determined by a curve fitting with the mean grade around **B+**

No time extension or make-up will be given to **tardy** or **absent** students for quiz and homework

No student will be excused from taking an exam without my **written permission**.

Class Policies

Students are expected to do their own quizzes, homework and examinations without group discussion or plagiarizing.

Any such **dishonorable acts** will be **reported immediately** to the Office of Academic Integrity of GWU.

You are always **encouraged** to report such activities to **me**, or to **Professor Michael M. King**, the chair of the Chemistry Department.

Your privacy will be strictly protected.

In case you are not satisfied with my teaching, please talk to me and provide your thoughts.
Your comments are always appreciated !

What is Quantum Mechanics ?

Quantum mechanics is the fundamental law of interactions between elementary particles.

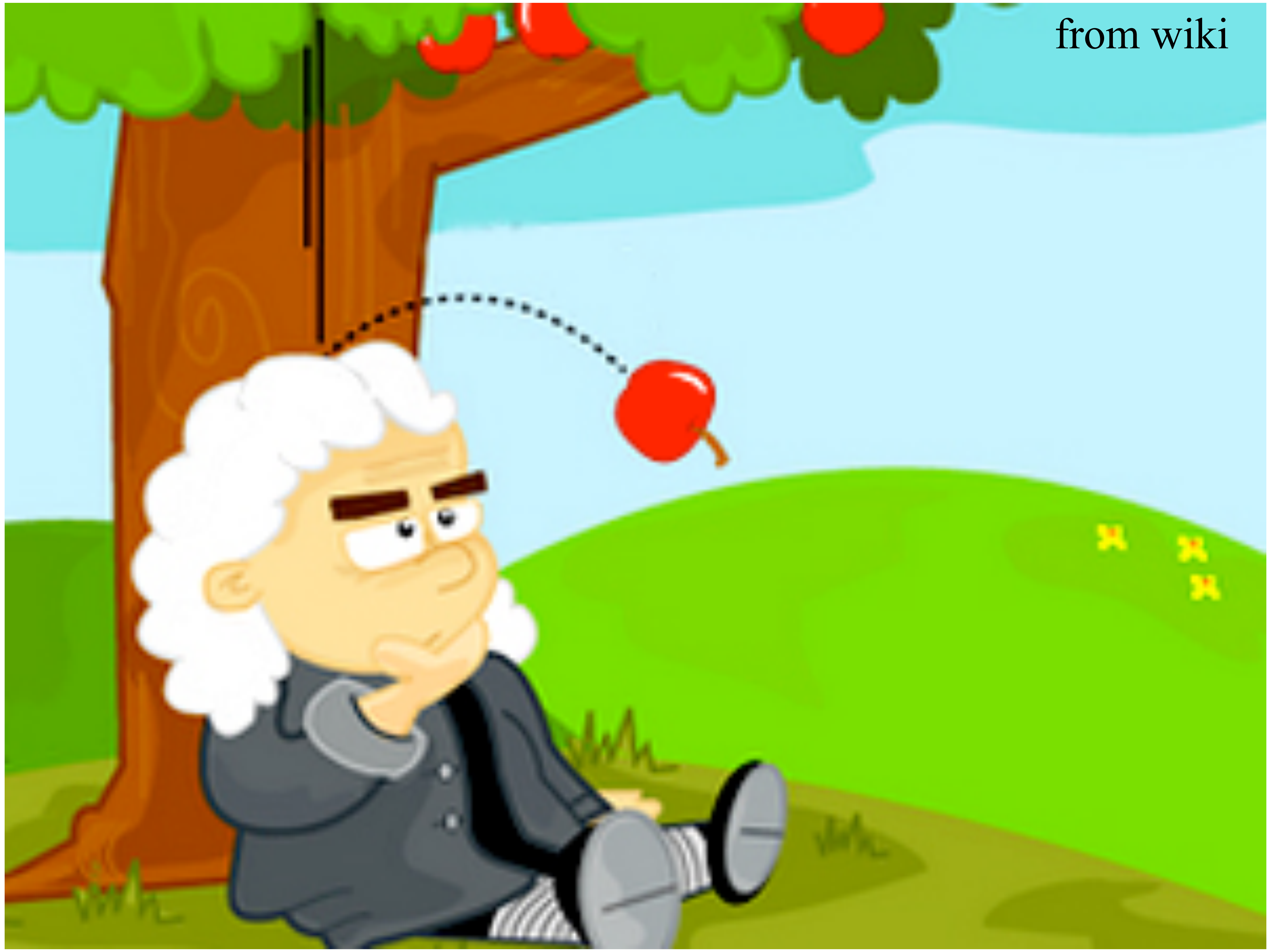
incomplete list of elementary particles (**61 in total**)

Fermions (half spin)	**6 quarks**	up, down, charge, strange, top, bottom (**fractional charge**)
	6 leptons	**electron**, electron neutrino, muon, muon neutrino, tau, tau neutrino (**integer charge**)
Bosons (integer spin)	photon, gluon, W boson, Z boson, **Higgs boson**	

Higgs boson: the **last** experimentally observed elementary particle

59-year wait for the creator of mass (God Particle)

History of Classical Mechanics



Newton's apple

Isaac Newton (1642-1727)

founder of Classical Mechanics

Newton's Law of Motion

$$F = ma = m\frac{dv}{dt} = m\frac{d^2x}{dt^2}$$

a particle's trajectory is deterministic

$$F(t) \to x(t)$$

a particle's presence is localized.

$$\delta x(t) = 0$$

a particle's response is instantaneous.

$$m\frac{d^2x(t)}{dt^2} = F(t')\delta(t - t')$$

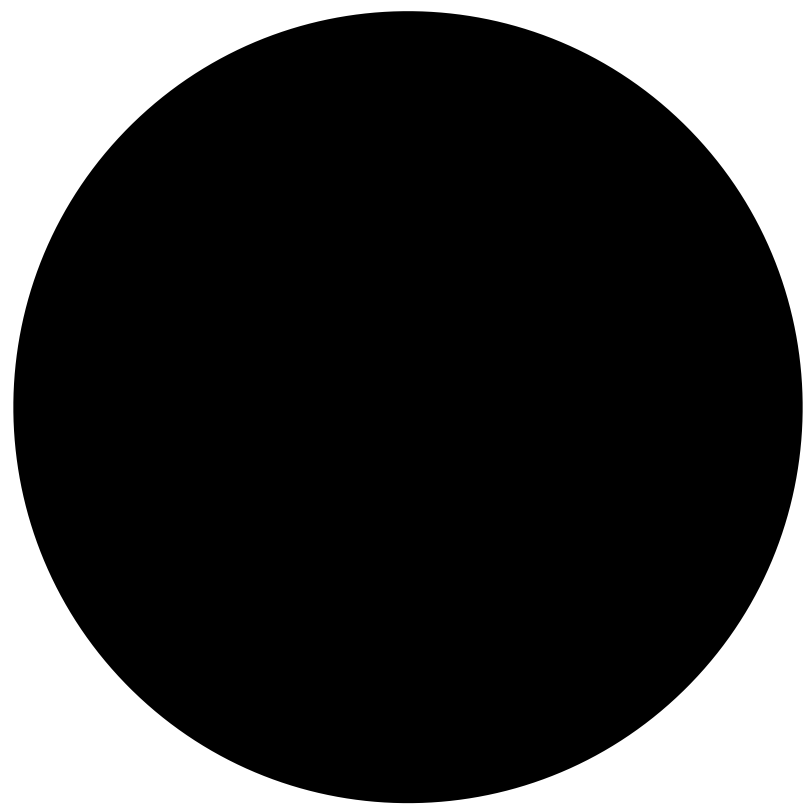
Supposedly Newton’s Apple Tree

Cambridge University Botanic Garden

Breakdown of Classical Mechanics

blackbody radiation

T≠0



infra-red $\longrightarrow$

T=300K

thermal energy ⇔ electromagnetic radiation

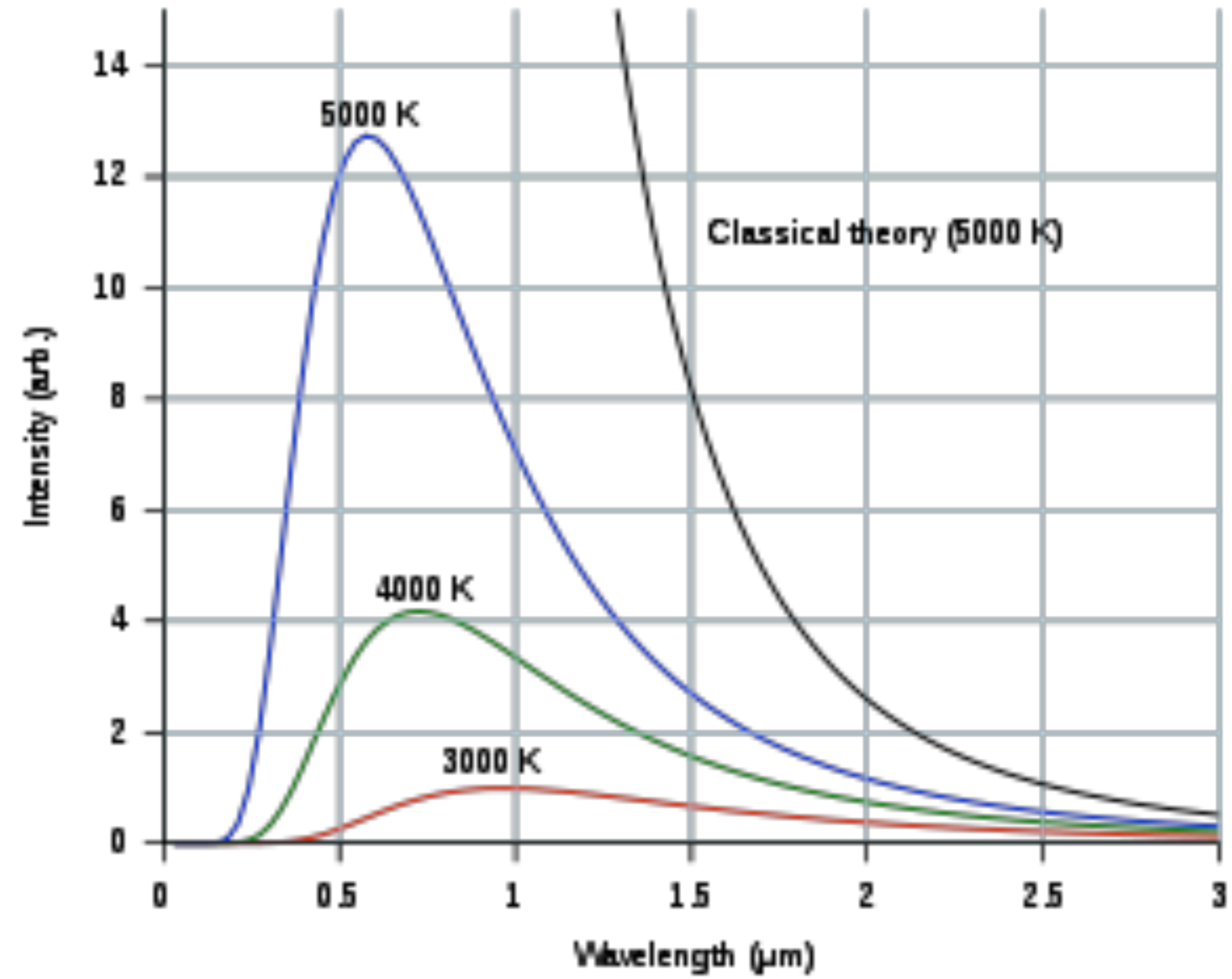
Classical Rayleigh-Jeans Law:

$$I_\lambda(T) = \frac{2ck_BT}{\lambda^4}$$

$$\boxed{\lambda \rightarrow 0, I \rightarrow \infty}$$???

what went wrong?

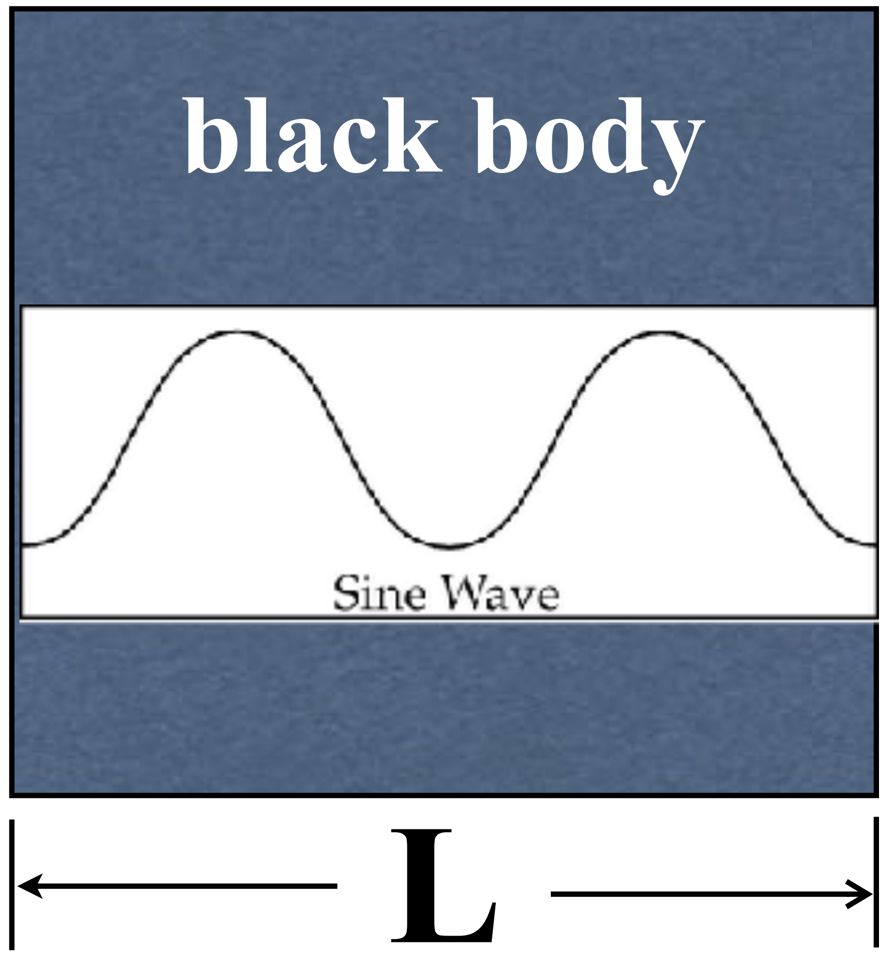
from wiki



Emission Intensity Profile

("ultraviolet catastrophe")

Derivation of Rayleigh-Jeans Law



$L \to \infty$: to ensure a **complete spectrum** of molecular vibrations

$$\lambda \in (0,\infty)$$

Under **thermal equilibrium**:

$$E = k_B T$$

all vibrational models have the **same** energy $k_B T$

regardless of their wavelengths

number of states: $g(\lambda) = \dfrac{8\pi}{\lambda^4} V$ $\longrightarrow$ **volume of a 3-D black body**

Total energy per unit volume, **energy density, for a given vibrational mode,**

$$U_{classical}(\lambda) = \frac{g(\lambda) k_B T}{V} = \frac{8\pi k_B T}{\lambda^4}$$

Planck's Law

Max Planck:
(1858-1947)

(1900)
Era of Quantum Mechanics

$$I_\lambda(T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/(\lambda k_B T)}-1}$$

Long Wavelength:

$$\lambda \to \infty, \frac{1}{e^{hc/(\lambda k_B T)}-1} \to \frac{\lambda k_B T}{hc}, \boxed{I_\lambda(T) \to \frac{2ck_B T}{\lambda^4}}$$

Rayleigh-Jeans Law

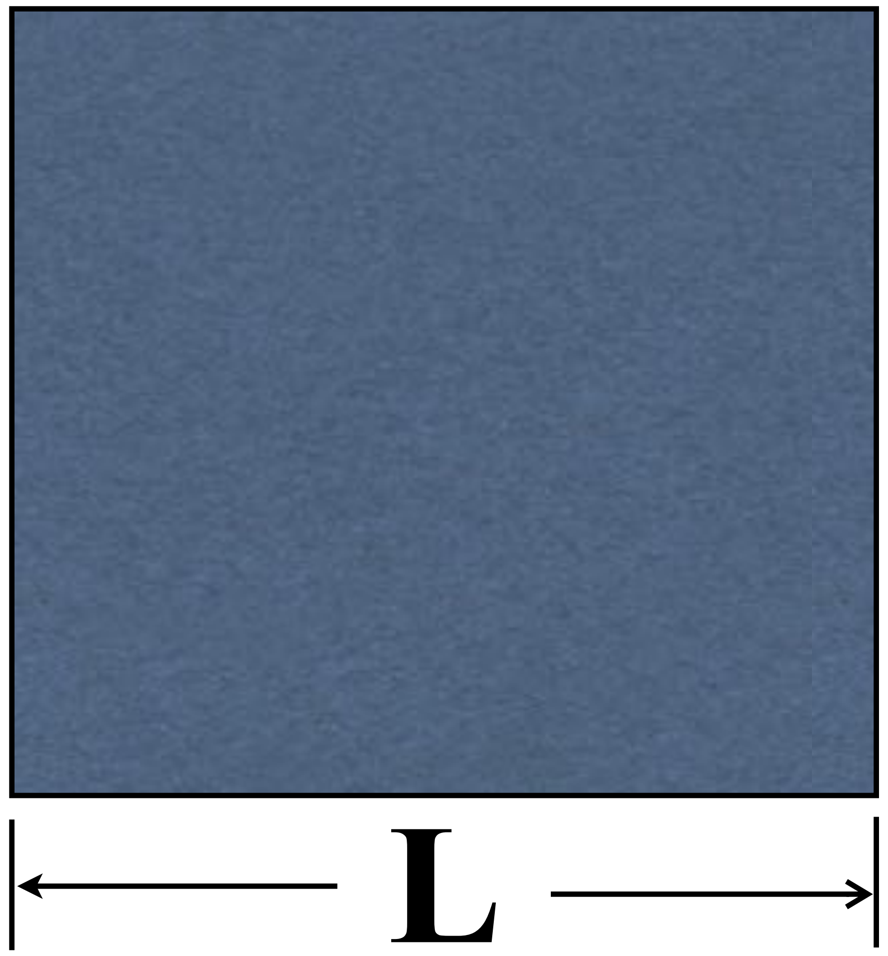
Short Wavelength:

$$\lambda \to 0, \frac{1}{e^{hc/(\lambda k_B T)}-1} \to e^{-\frac{hc}{\lambda k_B T}}, \boxed{I_\lambda(T) \to \frac{2hc^2}{\lambda^5}e^{-\frac{hc}{\lambda k_B T}}}$$

Wien Approximation

Perfect agreement with experiments is achieved !

Derivation of Planck's Law



$L \to \infty$: to ensure a **complete spectrum** of molecular vibrations

$$\omega = \frac{2\pi c}{\lambda} \qquad \omega \in (0, \infty) \qquad \hbar = \frac{h}{2\pi}$$

$h \longrightarrow$ planck constant $6.63 \times 10^{-34}\,\mathrm{m^2 kg/s}$

For a given vibration mode, **ω**, the allowed energies are **discrete**

$$E_n = n\hbar\omega \qquad \boxed{n : any \text{ postive integer}}$$

Under **thermal equilibrium**:

$$P_n(\omega) = \frac{e^{-\frac{E_n}{k_B T}}}{\boxed{\sum_{n=1}^{\infty} e^{-\frac{E_n}{k_B T}}}}$$

canonical partition function

zero point   0 *when* $T \to 0$

$$\langle E(\omega) \rangle = \sum_{n=1}^{\infty} E_n P_n(\omega) = \boxed{\frac{1}{2}\hbar\omega} + \boxed{\frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}} \quad U(T)$$

thermally averaged energy for a **quantized oscillator**

a quantum oscillator can **NOT** be entirely frozen !

Further Derivation of Planck's Law

density of states: $g(\omega) = \dfrac{\omega^2}{4c^2\pi^3}V \longrightarrow$ **volume of a 3-D black body**

How many oscillation modes are there within a given energy range, from $E - \frac{1}{2}\delta E$ to $E + \frac{1}{2}\delta E$?

Total energy per unit volume, **energy density, for a given vibrational mode,**

$$U_{quantum}(\omega) = \frac{g(\omega)E(\omega)}{V} = \boxed{\frac{\hbar\omega^3}{4c^2\pi^3\left(e^{\hbar\omega/k_BT} - 1\right)}}$$

convergent when $\omega \to \infty$

If the available energy levels are **continuous** as assumed by **classical mechanics**

$$U_{classical}(\omega) = \frac{g(\omega)k_BT}{V} = \boxed{\frac{\omega^2 k_BT}{4c^2\pi^3}}$$

divergent when $\omega \to \infty$

Rayleigh-Jeans Law

Classical Representation of an Elementary Particle

Newton's Second Law of Motion:

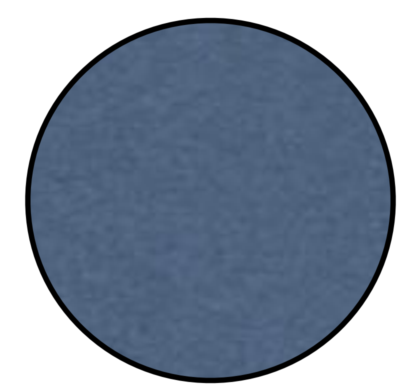
$$\vec{F} = m\vec{a} = m\frac{d\vec{v}}{dt} = m\frac{d^2\vec{r}}{dt^2}$$

$\rightarrow$: vector

$\vec{r}(x,y,z)$

How much information is needed to **uniquely quantify** a single particle's state in ***classical mechanics***?

potential energy



kinetic energy

1. position $\vec{r}(x,y,z)$

2. velocity $\vec{v}\left(\frac{dx}{dt},\frac{dy}{dt},\frac{dz}{dt}\right)$

$$S = S(\vec{r},\vec{v})$$ (classical equation of state)

How much information is needed to **uniquely quantify** a single particle's state in ***quantum mechanics***?

Wave-Particle Duality

*"For matter, just much as for radiation, in particular **light**, we must introduce at one and the same time the **corpuscle** concept and the **wave** concept?"*

— ***Louis de Broglie***, 1929, Nobel Prize Speech

wave-particle duality

***de Broglie* relation**

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

the ***wavelength*** of a **particle** ⟵ λ

h ⟶ Planck constant $6.63\times 10^{-34}\, m^2 kg/s$

$p = mv$

p ⟶ the ***momentum*** of a **wave**

heavy, fast particle $\vec{p}$

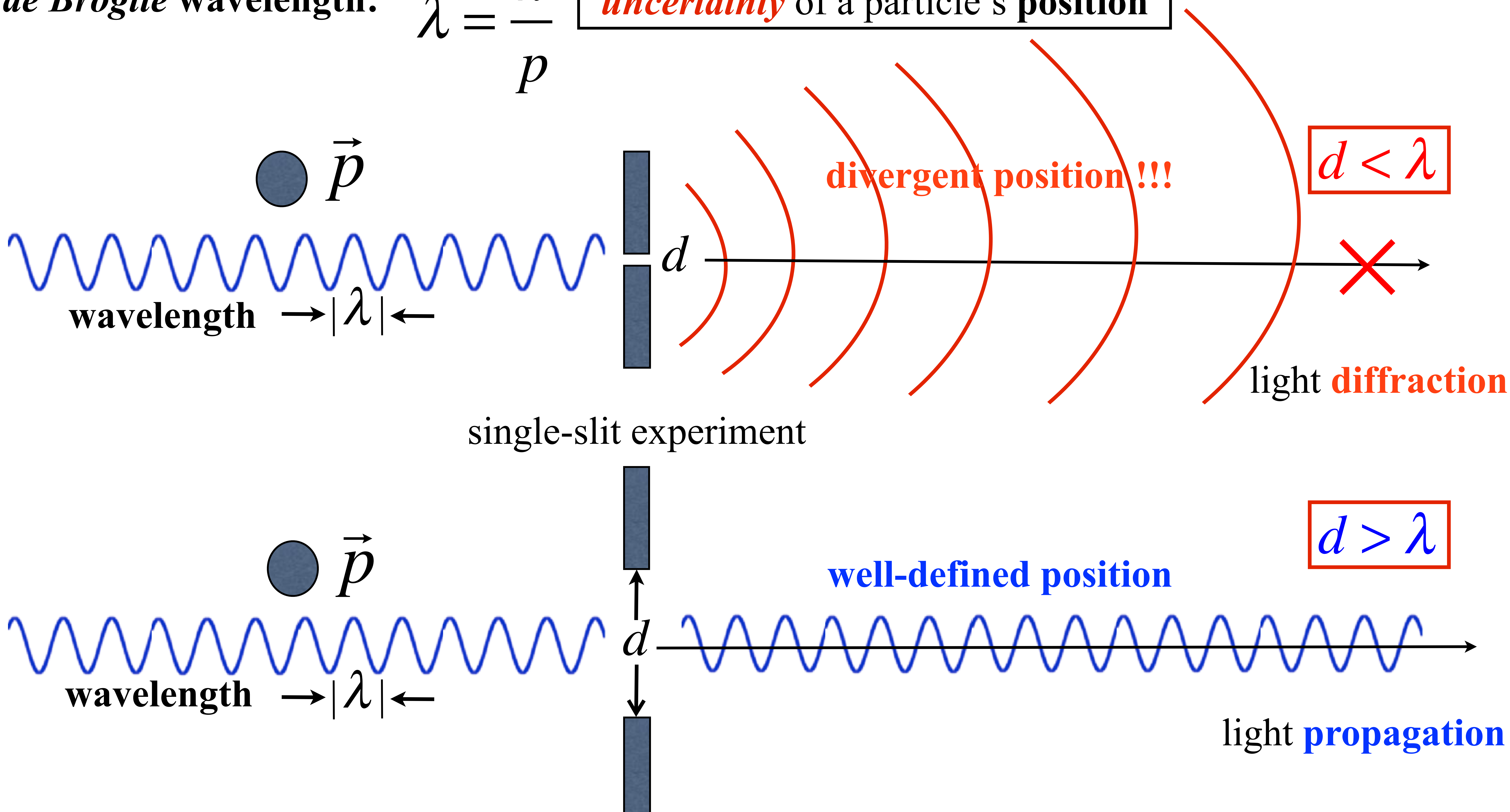
short wavelength $\rightarrow|\lambda|\leftarrow$

light, slow particle $\vec{p}$

long wavelength $|\leftarrow \lambda \rightarrow|$

Physical Meaning of de Broglie Wavelength

***de Broglie* wavelength:** $\lambda = \dfrac{h}{p}$ $\boxed{\textit{uncertainty} \text{ of a particle's } \textbf{position}}$



Uncertainty of a Particle's Position

You can reduce your own spatial uncertainty by running fast !

The world's **fastest** man:

Usain Bolt (Jamica)
100-meter world's record:
9.58 second

August 16th, 2009 Berlin, Germany

Mr. Bolt weights **210 pounds** (95 kilograms)

What is the de Broglie's wavelength of Mr. Bolt?

$$\lambda_{Bolt} = \frac{h}{p_{Bolt}} = \frac{h}{m_{Bolt} \times V_{Bolt}} = \frac{6.63 \times 10^{-34}}{95 \times \dfrac{100}{9.58}}$$

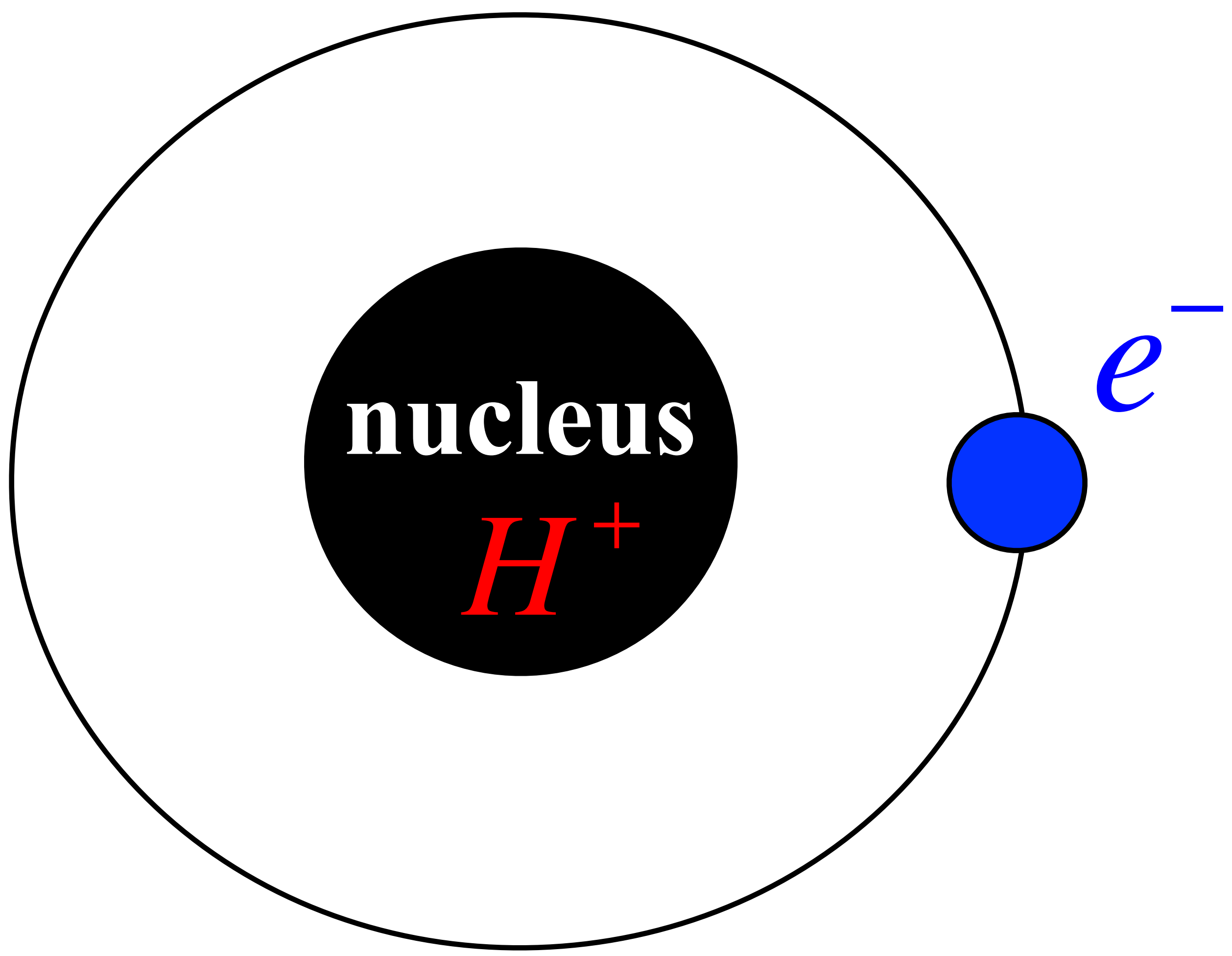
$$\lambda_{Bolt} = 6.69 \times 10^{-37}\, meter$$

Mr. Bolt's spatial uncertainty is negligible !

$$6.69 \times 10^{-37}\, meter \ll 100\ meter$$

the Importance of de Broglie Wavelength

The de Broglie wavelength of **an electron**:



hydrogen atom

at ground state, the kinetic energy of the electron:

$$E_k = 13.6\ eV$$

the mass of electron:

$$m_e = 9.109 \times 10^{-31} kg$$

what is the electron's de Broglie wavelength?

$$\lambda_e = \frac{h}{p_e} = \frac{h}{m_e v_e} = \frac{h}{\sqrt{2E_k m_e}}$$

$$E_k = \frac{1}{2} m_e v_e^2$$

$$\lambda = ?$$

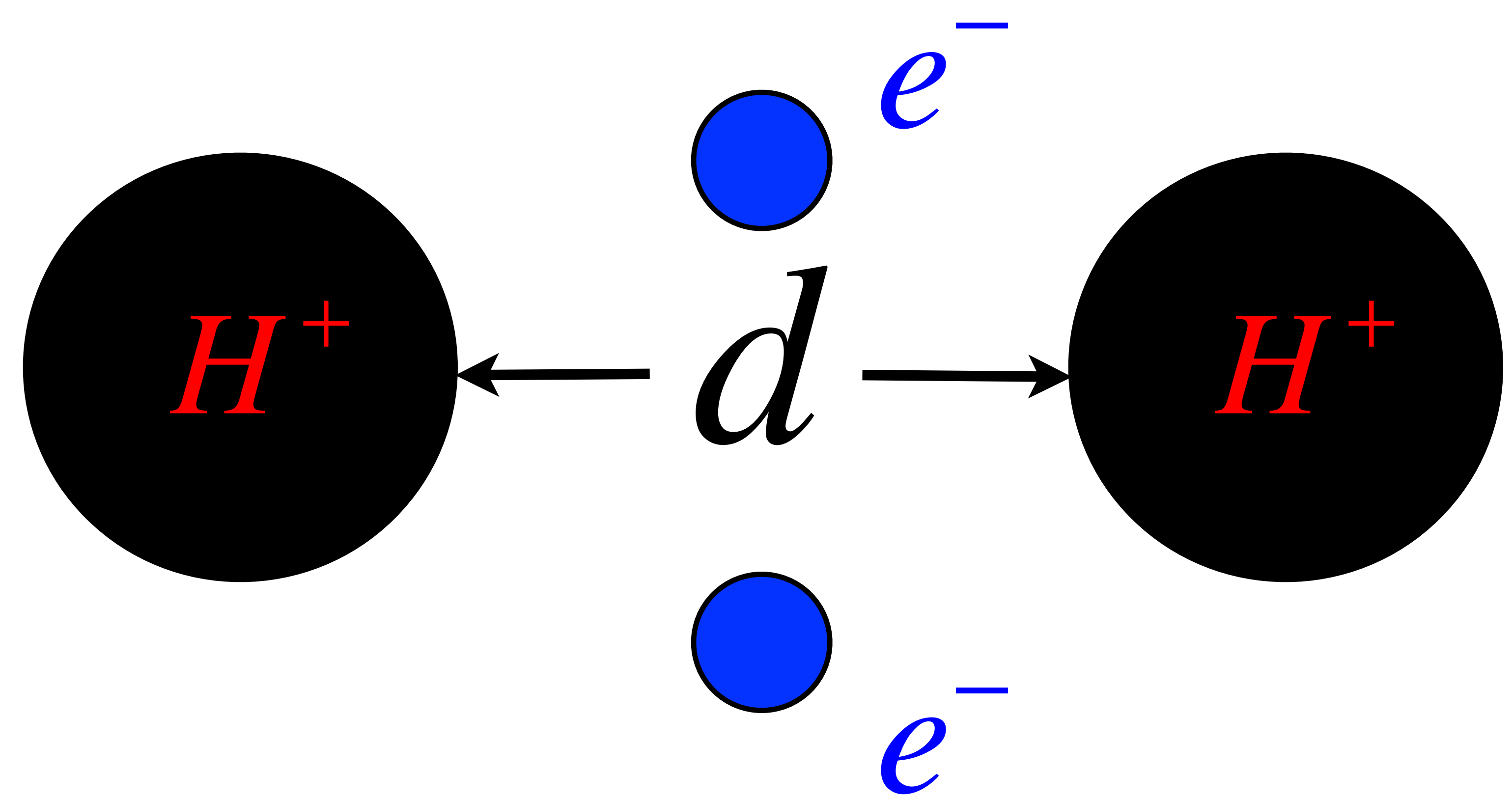
$$\lambda = 3.32 \times 10^{-10} meter = 3.32 \text{Å}$$

Does it matter?

Delocalization Characteristics of Elementary Particles

H-H bond length:

$$d = 0.74\mathring{A}$$



hydrogen molecule H_2

spatial uncertainty of an electron

$$\lambda_e = 3.32\mathring{A}$$

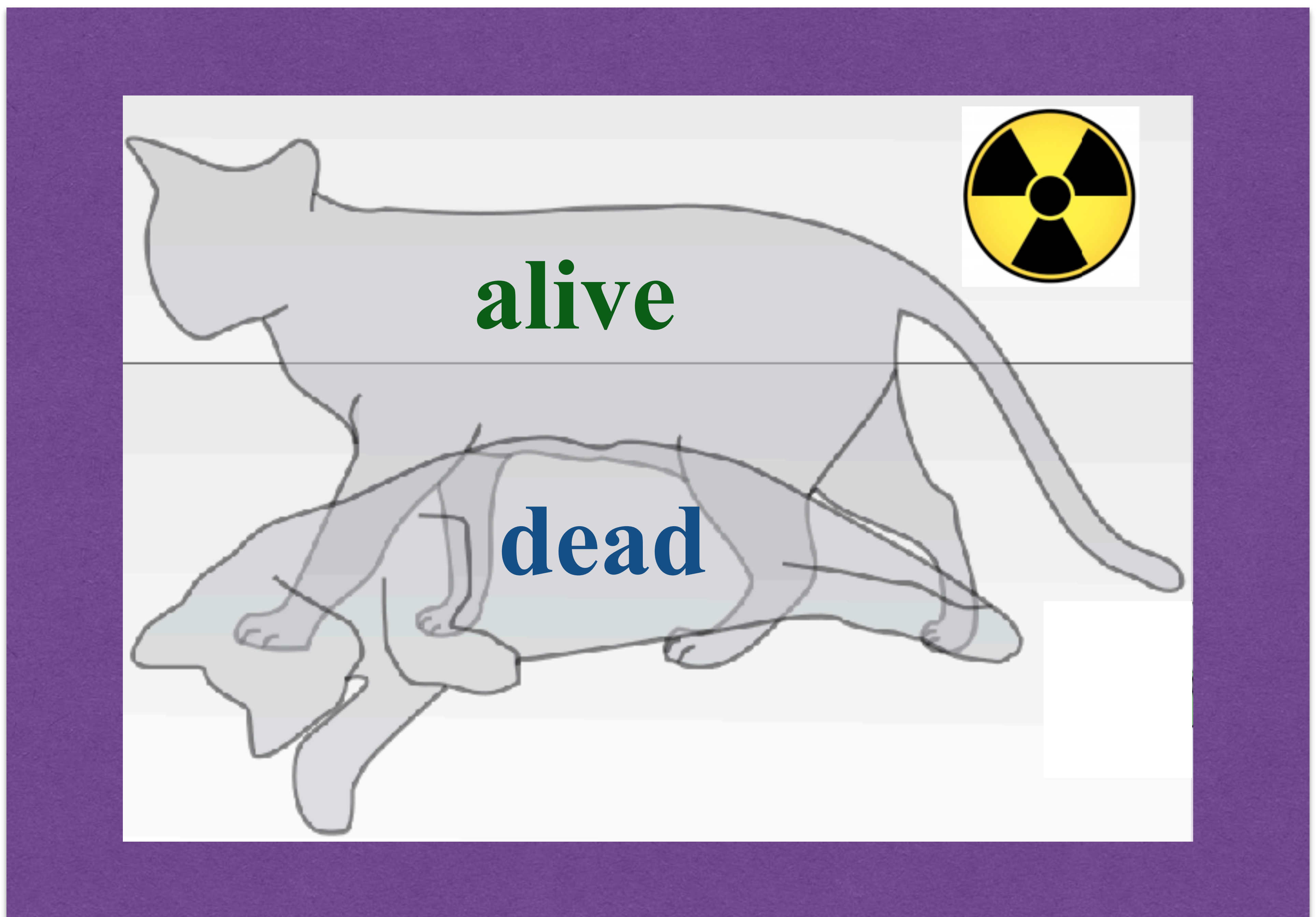
$$\boxed{d < \lambda_e}$$

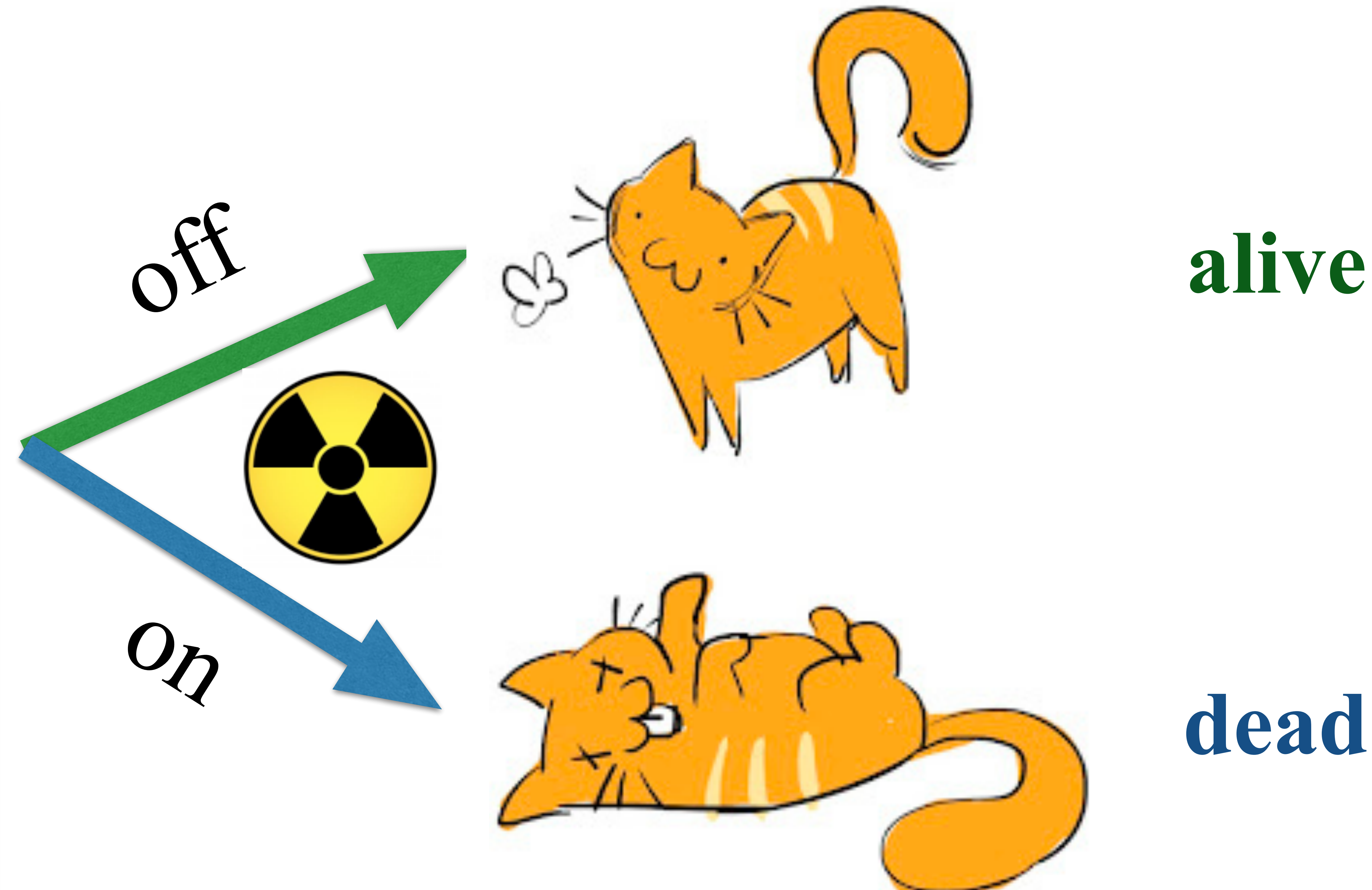
It is even impossible to tell which atom owns which electron !!!

It would be more appropriate to describe an elementary particle by a ***delocalized wave*** rather than by a ***localized particle.***

Schrödinger's Cat

The **uncertainty** principle is applicable to **any** property of a physical object



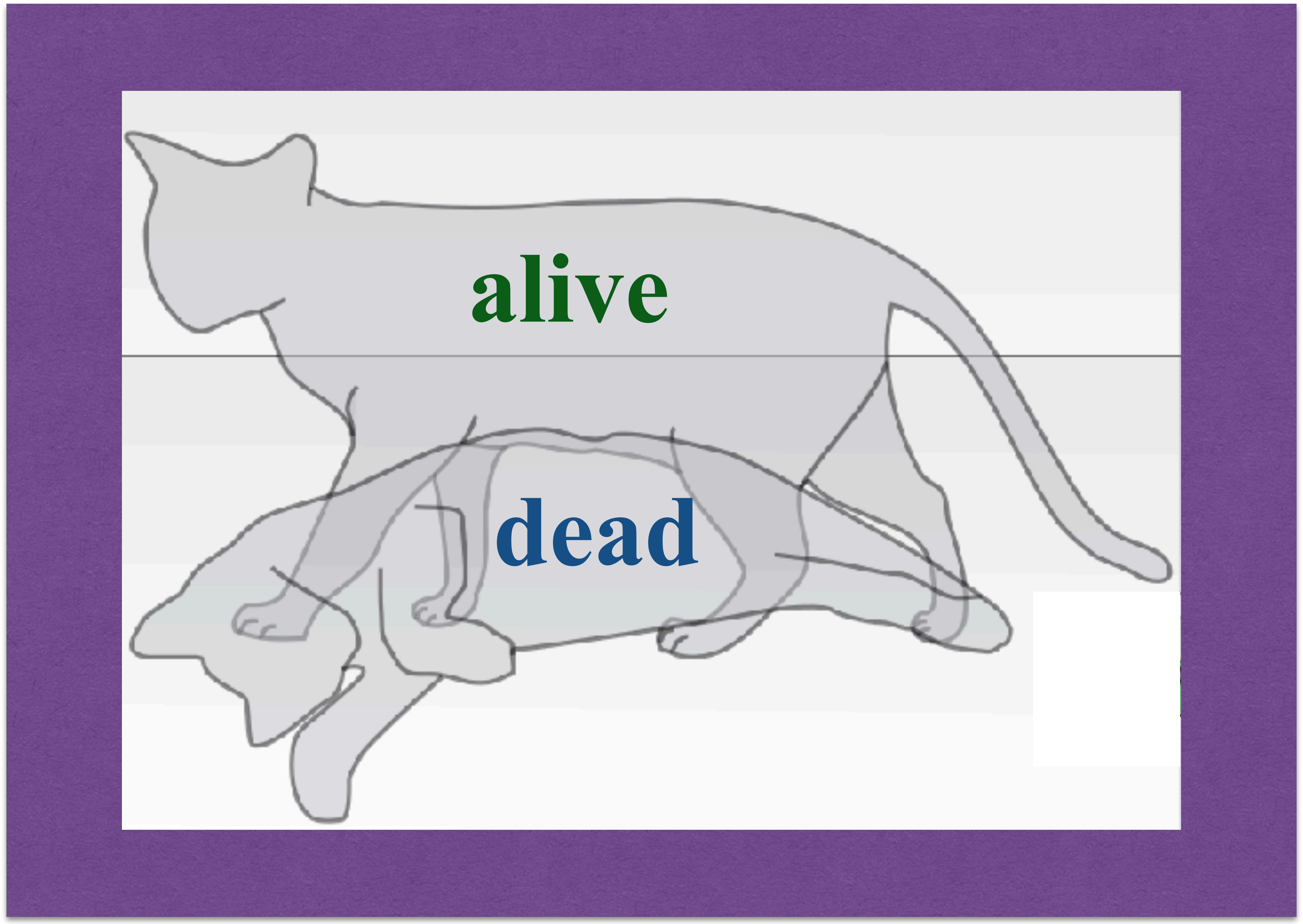


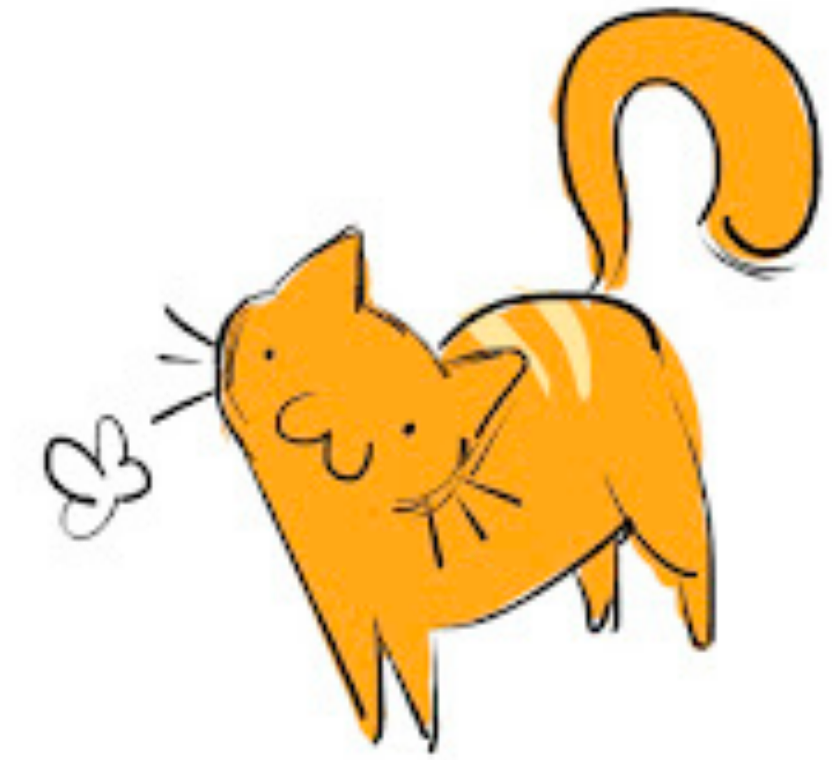
a **cat** trapped in a ***sealed*** box

50% on and 50% off

How likely will you observe an **alive** (or **dead**) cat?

Timing is Important





100%
alive

100%
dead

before ← → ***after***

50% alive + 50% dead

superposition

measurement

either 100% **alive**
or 100% **dead**

wavefunction collapse

Superposition and Decoherence

courtesy of University of Paris XI

Homework 1

Reading assignment: **Chapter 1**

Homework assignment: **Problems 1.2, 1.13**

Homework assignments must be turned in by **5:00 PM, August 30th, Wednesday**

to my mailbox in the Department Main Office
located at **Room 4500, Science and Engineering Hall**