1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2012

Part II – Quantum Mechanical Methods : Lecture 1

It's A Quantum World: The Theory of Quantum Mechanics

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3.021 Content Overview

I. Particle and continuum methods

1. Atoms, molecules, chemistry
2. Continuum modeling approaches and solution approaches
3. Statistical mechanics
4. Molecular dynamics, Monte Carlo
5. Visualization and data analysis
6. Mechanical properties – application: how things fail (and how to prevent it)
7. Multi-scale modeling paradigm
8. Biological systems (simulation in biophysics) – how proteins work and how to model them

II. Quantum mechanical methods ⟵ ***we are here***

Welcome to Part 2!

The next 11 lectures will cover atomistic quantum modeling of materials.

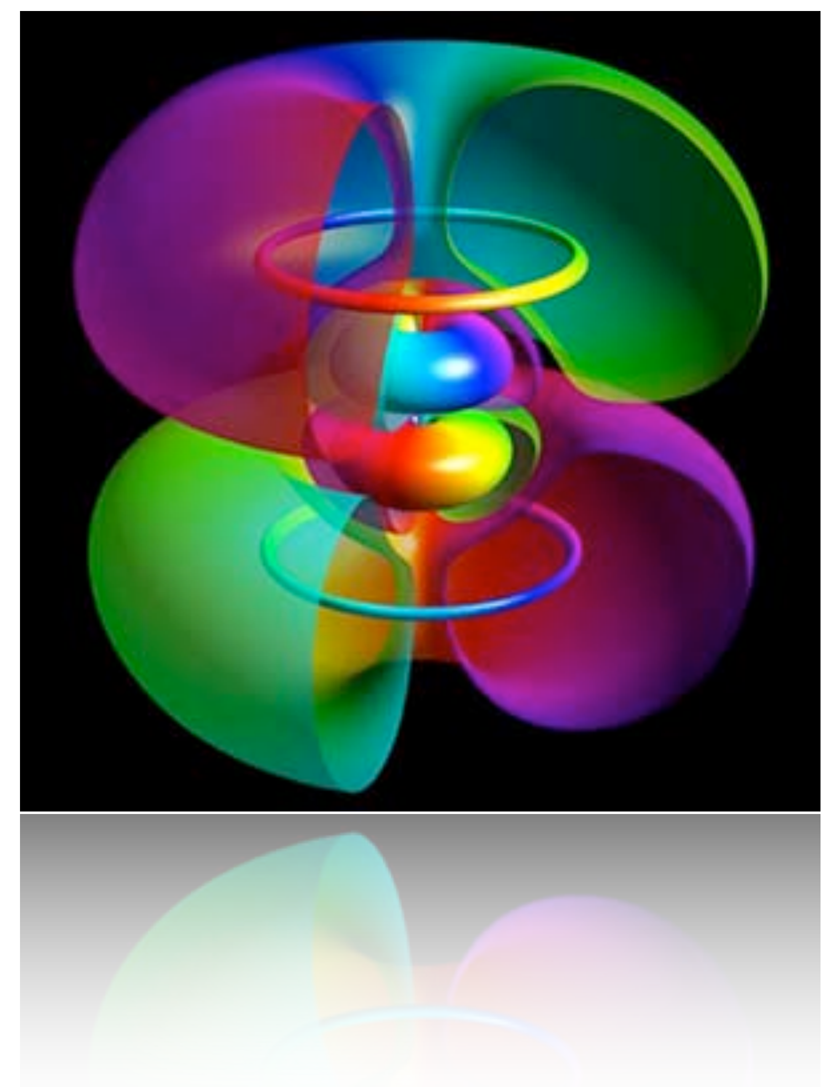
Note: there will be a substitute lecturer on Tuesday, April 10 and no class on Thursday, April 12.

Part II Topics

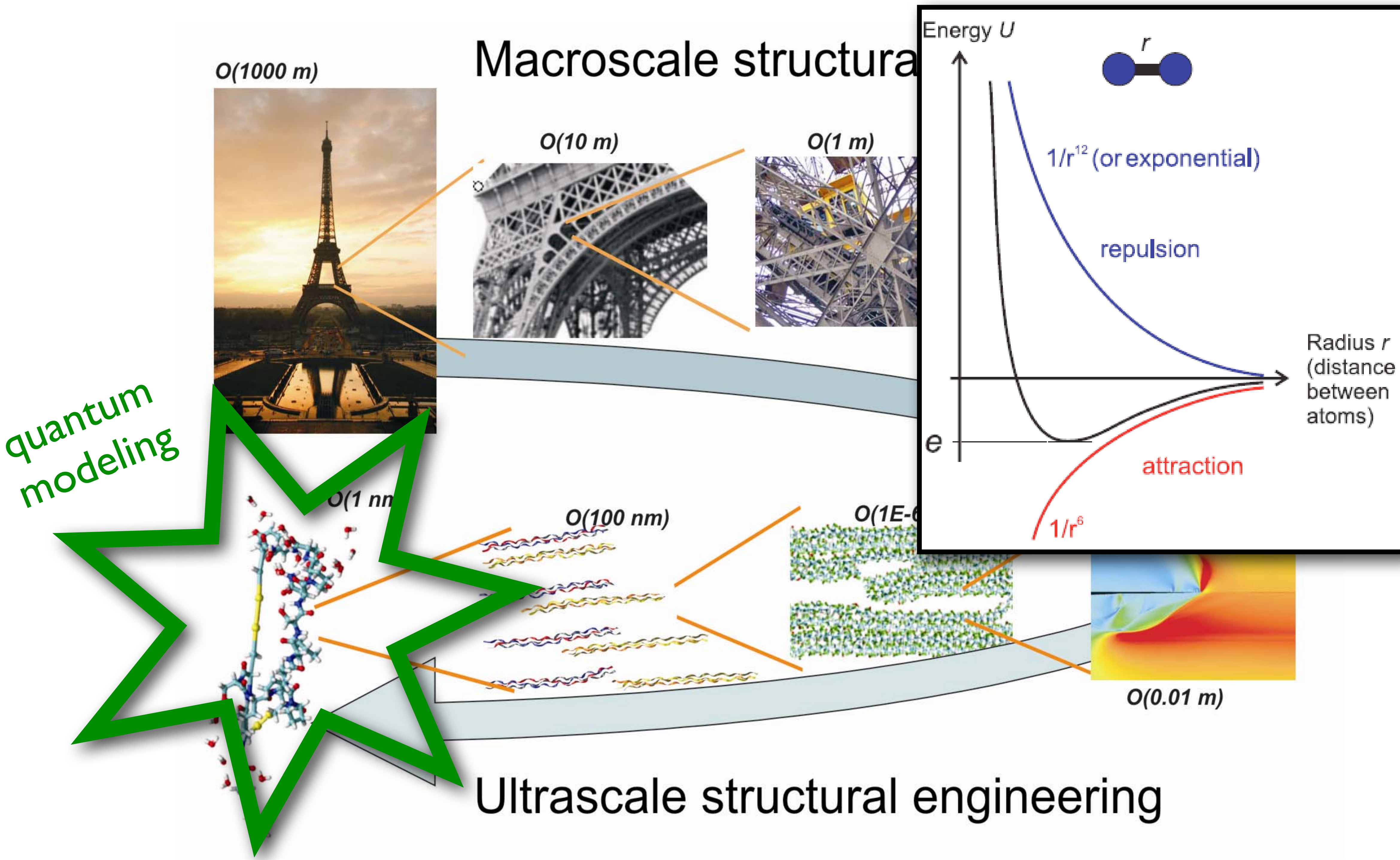
1. It's a Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. From Many-Body to Single-Particle; Quantum Modeling of Molecules
4. Application of Quantum Modeling of Molecules: Solar Thermal Fuels
5. Application of Quantum Modeling of Molecules: Hydrogen Storage
6. From Atoms to Solids
7. Quantum Modeling of Solids: Basic Properties
8. Advanced Prop. of Materials: What else can we do?
9. Application of Quantum Modeling of Solids: Solar Cells Part I
10. Application of Quantum Modeling of Solids: Solar Cells Part II
11. Application of Quantum Modeling of Solids: Nanotechnology

Lesson outline

- Why quantum mechanics?
- Wave aspect of matter
- Interpretation
- The Schrödinger equation
- Simple examples



Multi-scale modeling



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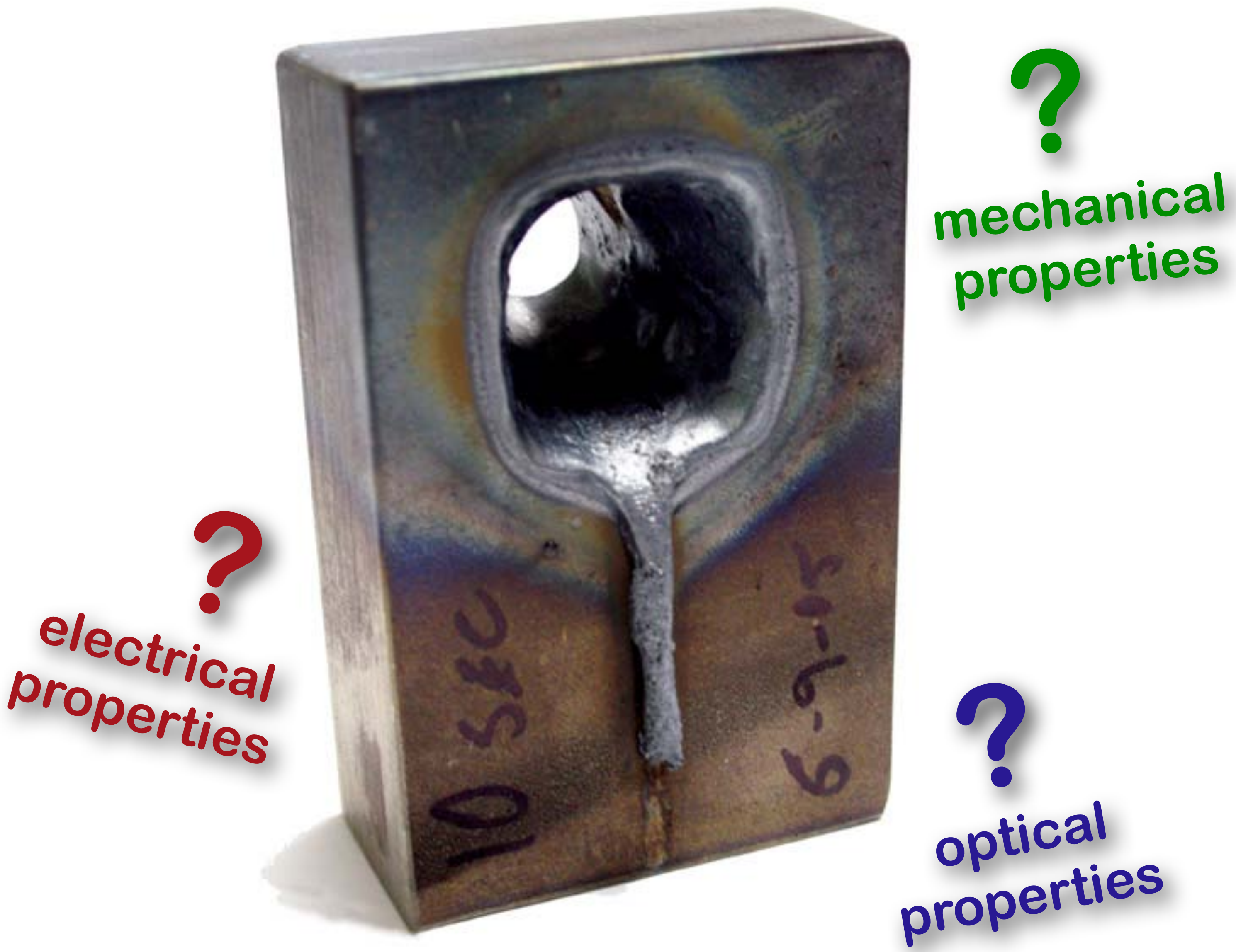
It's a quantum world!

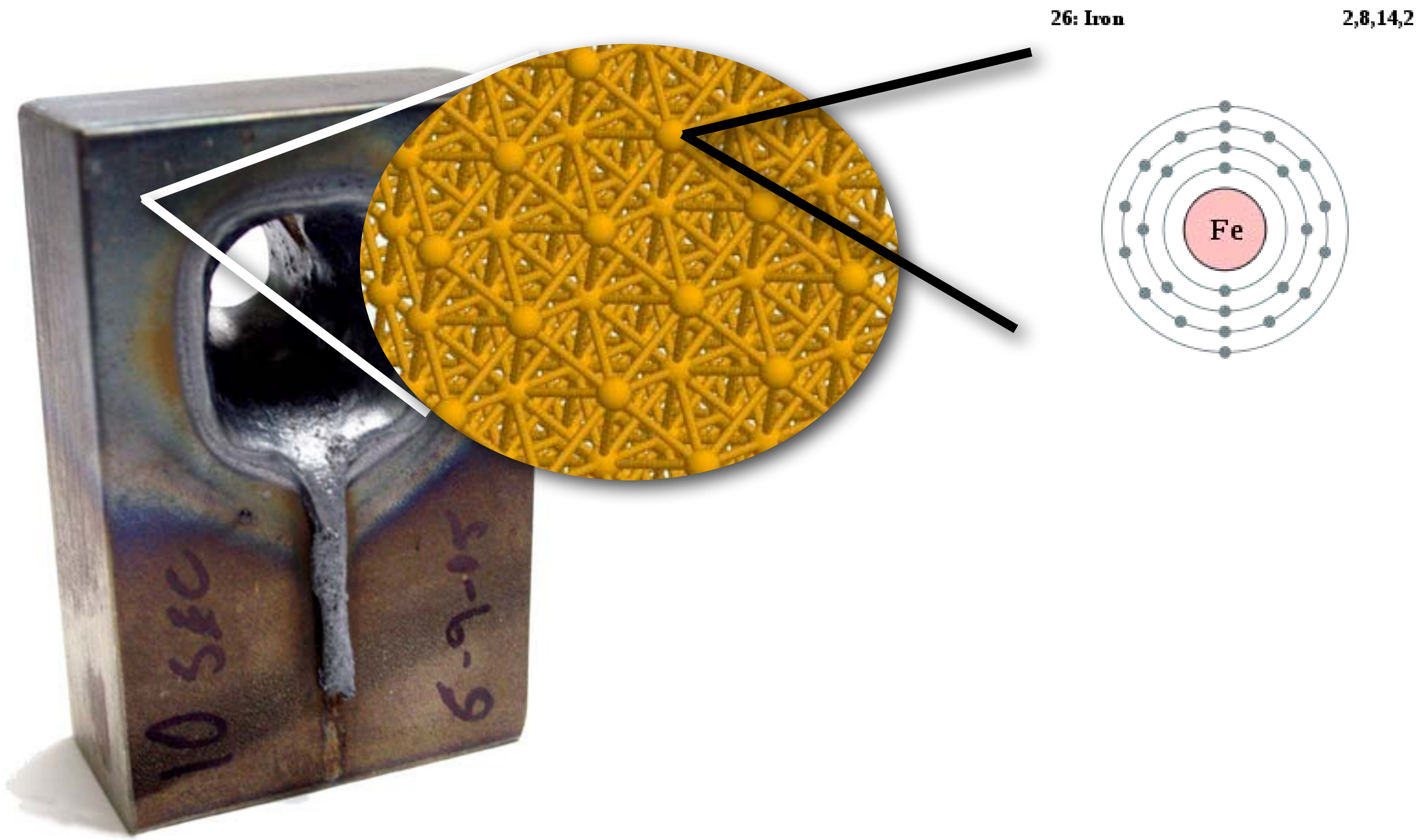
Motivation

If we understand **electrons**,
then we understand ***everything***.
(almost) ...

Quantum modeling/ simulation



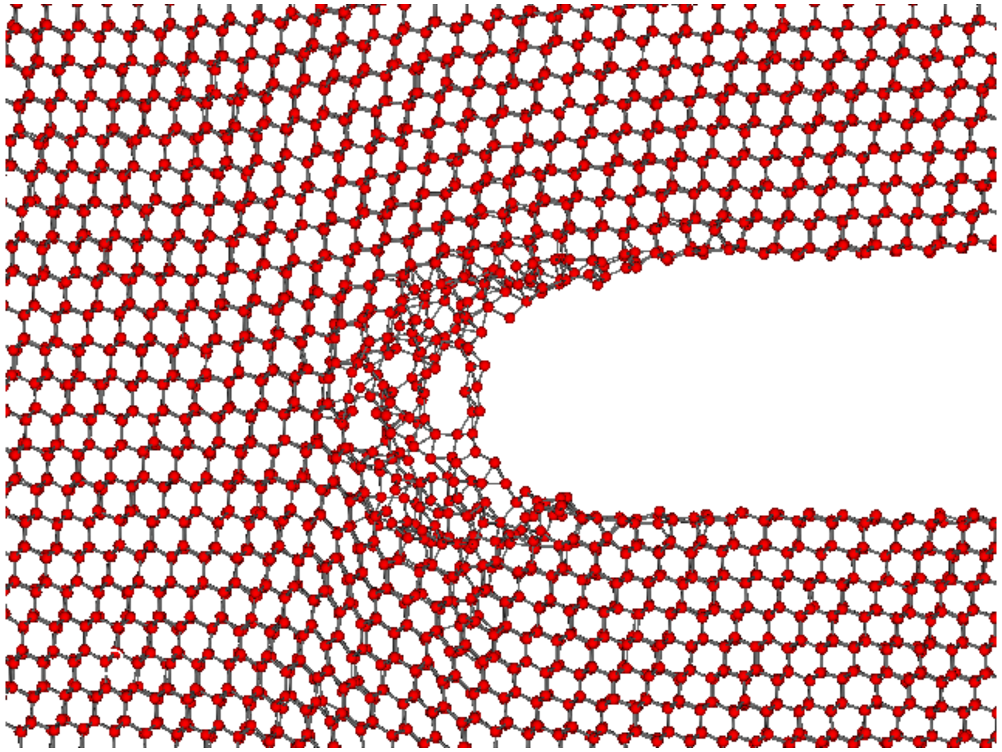
A simple iron atom ...



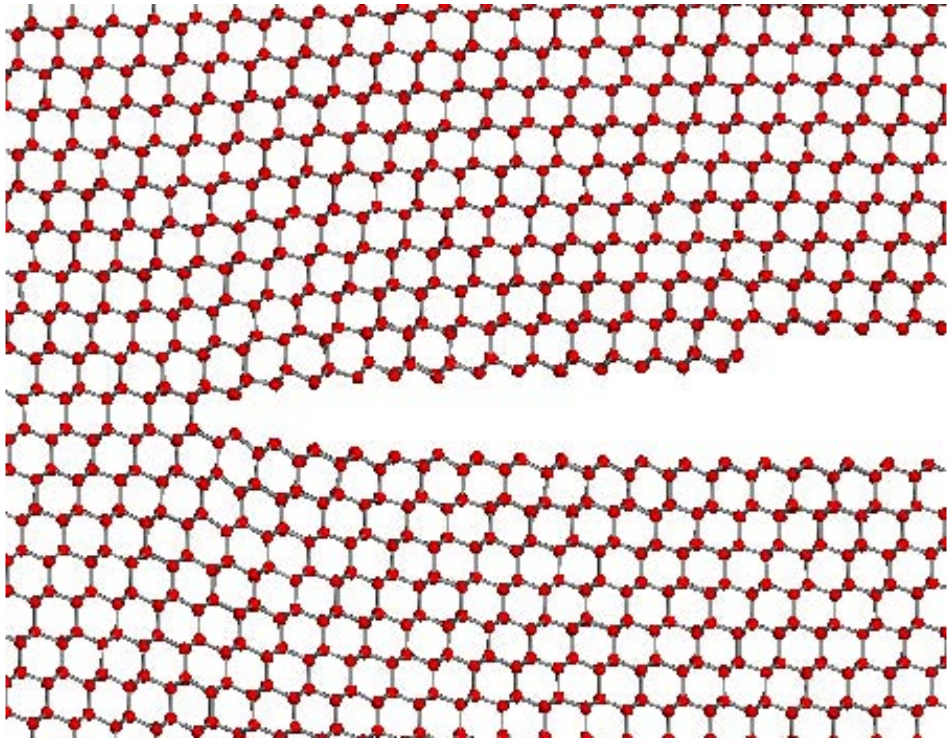
Why Quantum Mechanics?

Accurate/predictive structural/atomistic properties, when we need to span a wide range of coordinations, and bond-breaking, bond-forming takes place.

(But beware of accurate energetics with poor statistics !)



EDIP Si potential

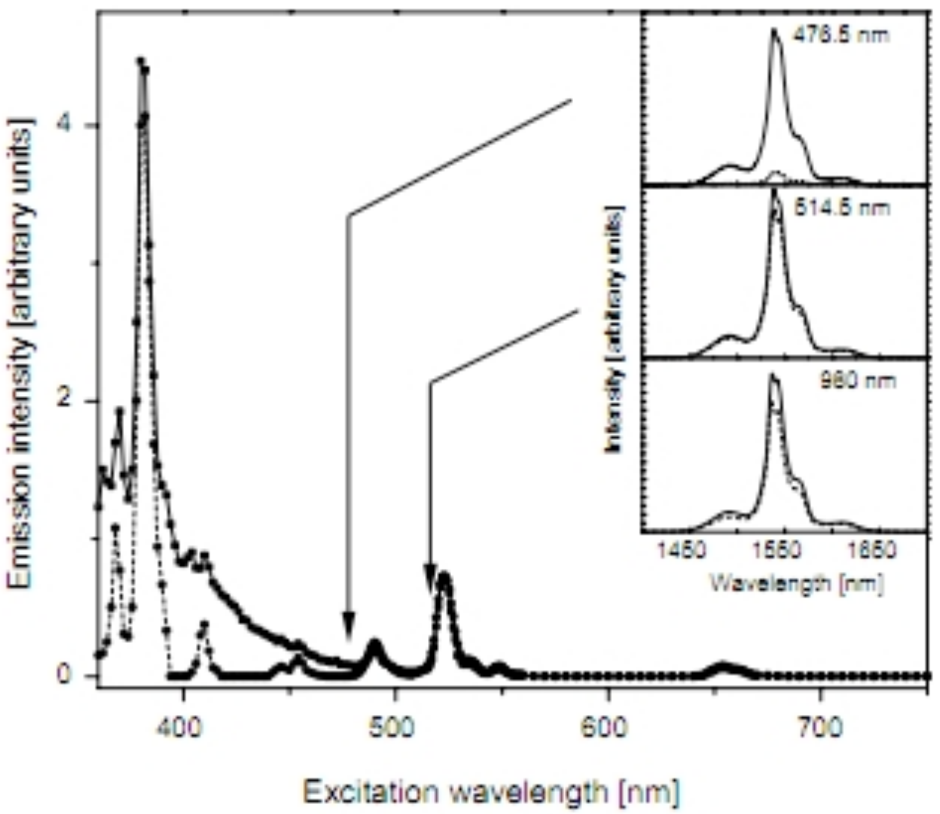


Tight-binding

Electronic, optical, magnetic properties

Image removed due to copyright restrictions. Please see Vangberg, T. R. Lie, and A. Ghosh. "Symmetry-Breaking Phenomena in Metalloporphyrn in Pi-Cation Radicals."

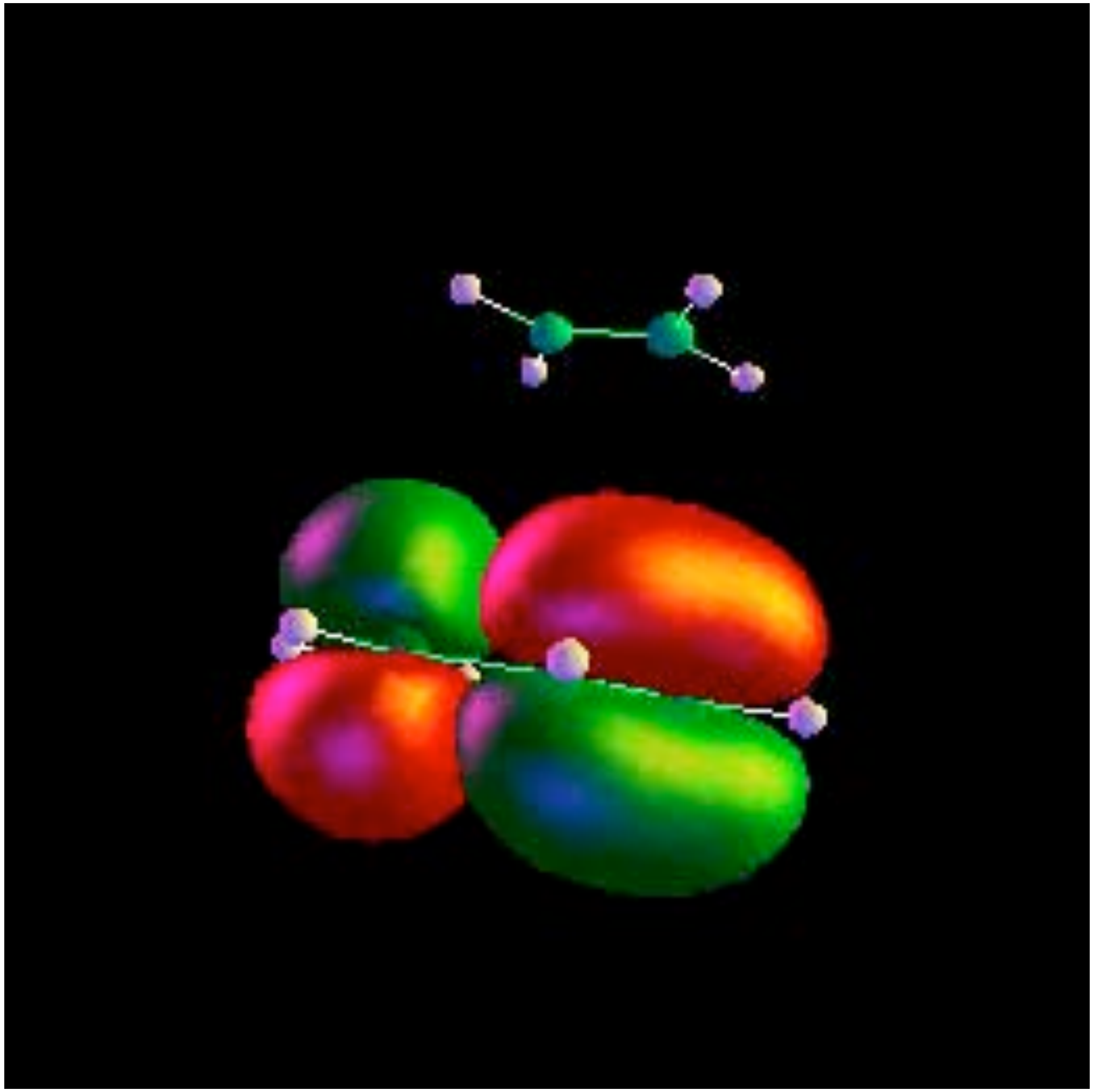
Jahn-Teller effect in porphyrins (A. Ghosh)



Non-resonant Raman in silicates (Lazzeri and Mauri)

Reactions

1,3-butadiene + ethylene → cyclohexene



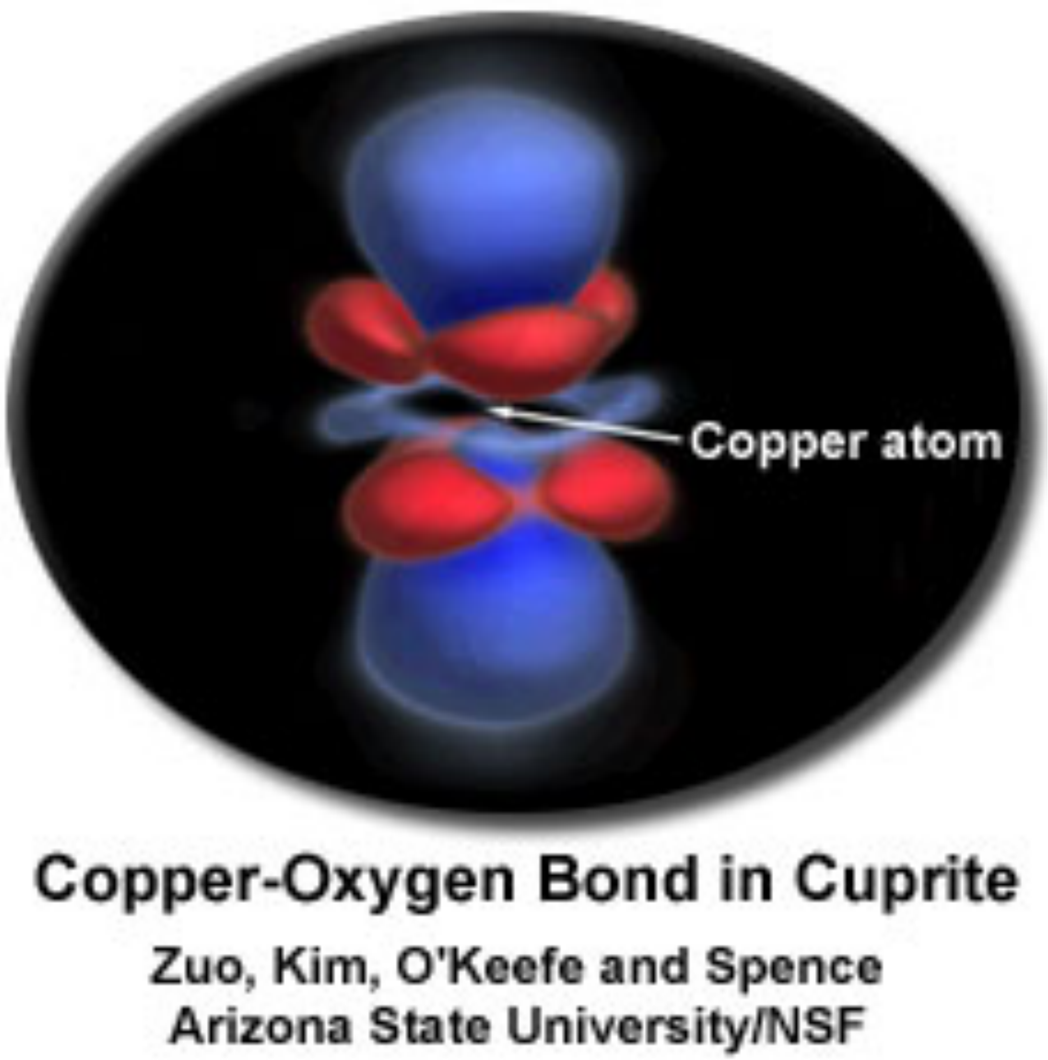
Standard Model of Matter

- Atoms are made by MASSIVE, POINT-LIKE NUCLEI (protons+neutrons)

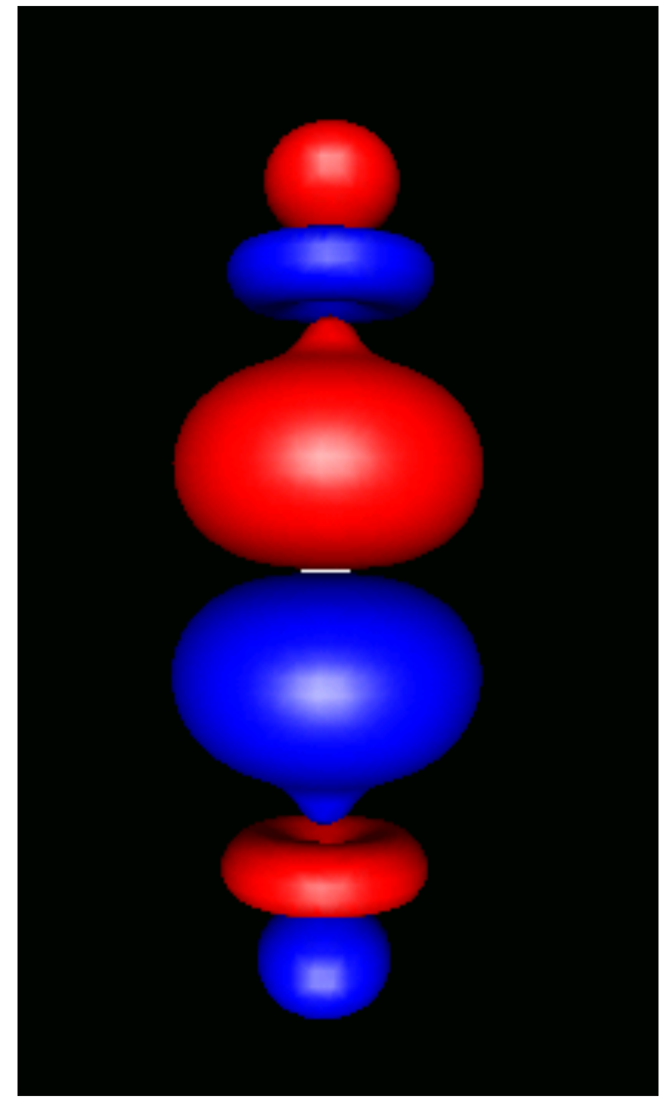
- Surrounded by tightly bound, rigid shells of CORE ELECTRONS

- Bound together by a glue of VALENCE ELECTRONS (gas vs. atomic orbitals)

It's real!



Cu-O Bond
(experiment)



Ti-O Bond
(theory)

Importance of Solving for this Picture with a Computer

- It provides us microscopic understanding
- It has predictive power (it is "first-principles")
- It allows controlled "gedanken" experiments
- Challenges:
  - Length scales
  - Time scales
  - Accuracy

Why quantum mechanics?

Classical mechanics

Newton's laws (1687)

$$\vec{F} = \frac{d(m\vec{v})}{dt}$$

Problems?

Why quantum mechanics?

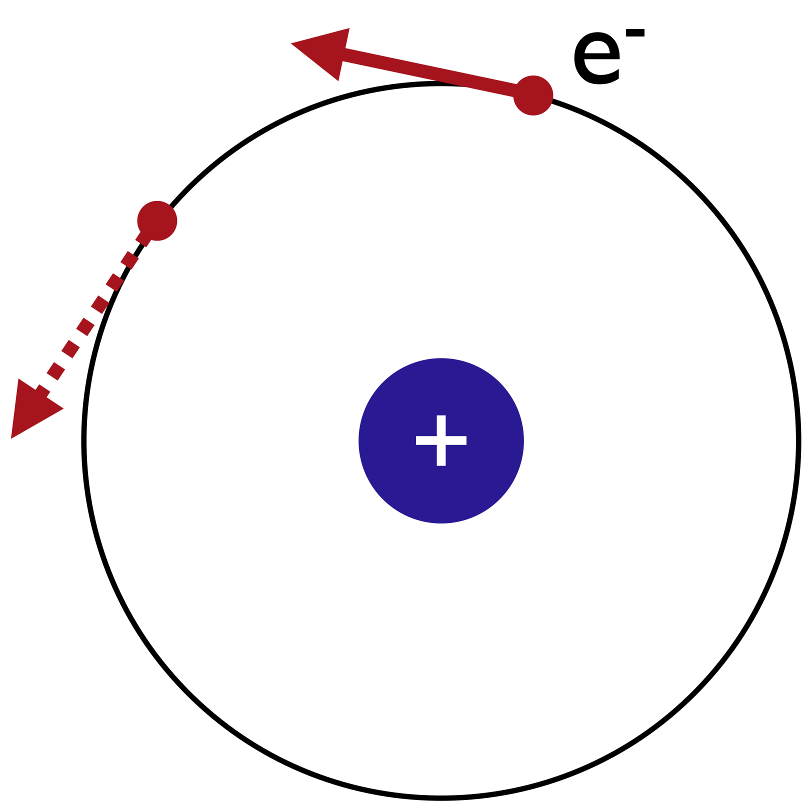
Problems in classical physics that led to quantum mechanics:

- “classical atom”
- quantization of properties
- wave aspect of matter
- (black-body radiation), ...

Quantum mechanists

Werner Heisenberg, Max Planck,
Louis de Broglie, Albert Einstein,
Niels Bohr, Erwin Schrödinger,
Max Born, John von Neumann,
Paul Dirac, Wolfgang Pauli
(1900 - 1930)

“Classical atoms”

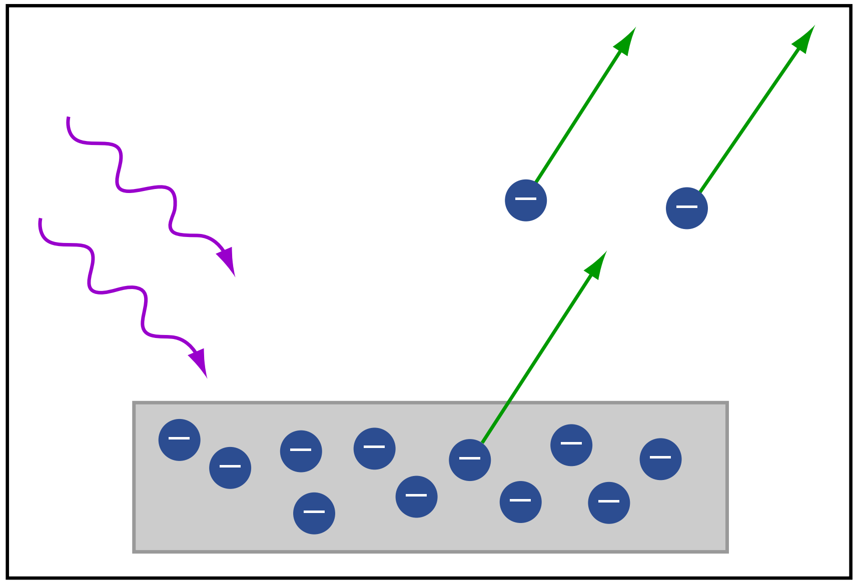


hydrogen atom

problem:
accelerated charge causes radiation, atom is not stable!

Quantization of properties

photoelectric effect



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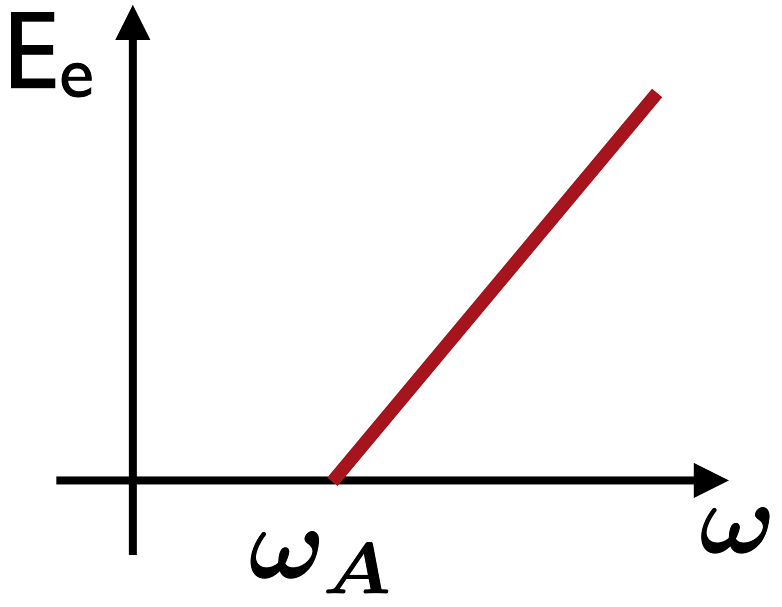


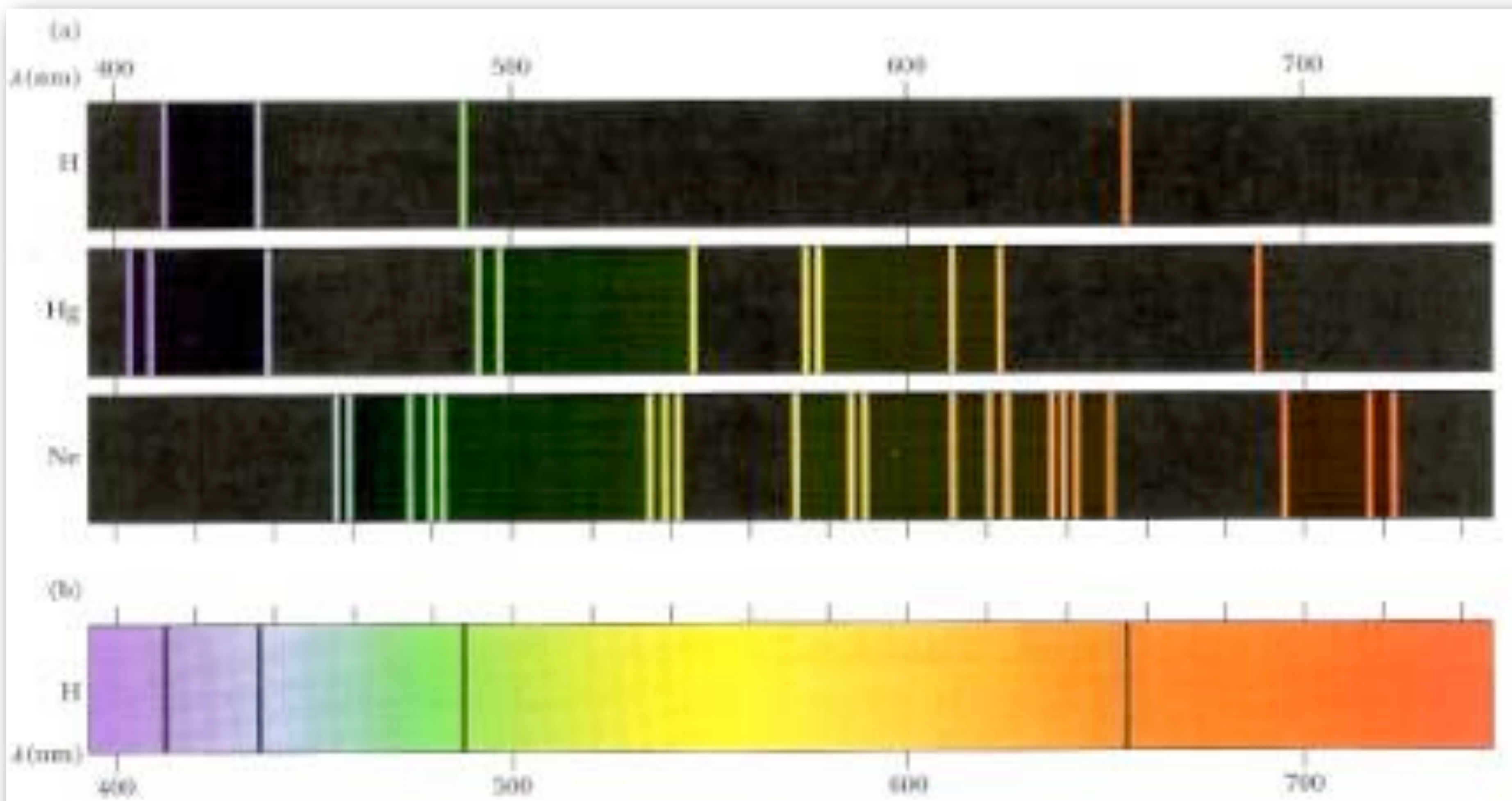
$$E = \hbar(\omega - \omega_A) = h(\nu - \nu_A)$$

$$h = 2\pi\hbar = 6.6 \cdot 10^{-34}\ \mathrm{Wattsec.}^2$$

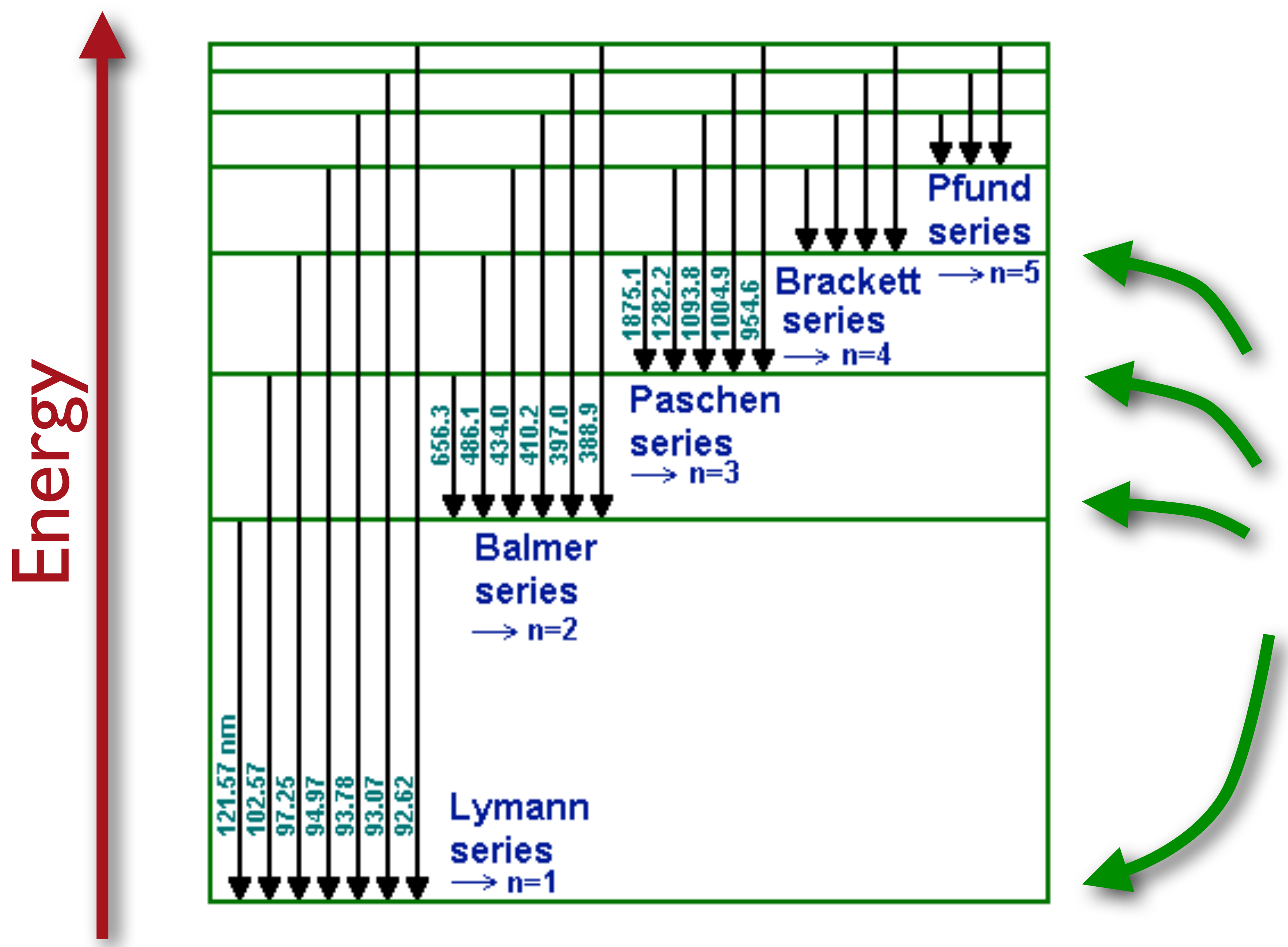
Einstein: photon $E = \hbar\omega$

Quantization of properties

atomic spectra



Quantization of properties



$$E = \hbar\omega$$

possible energy states

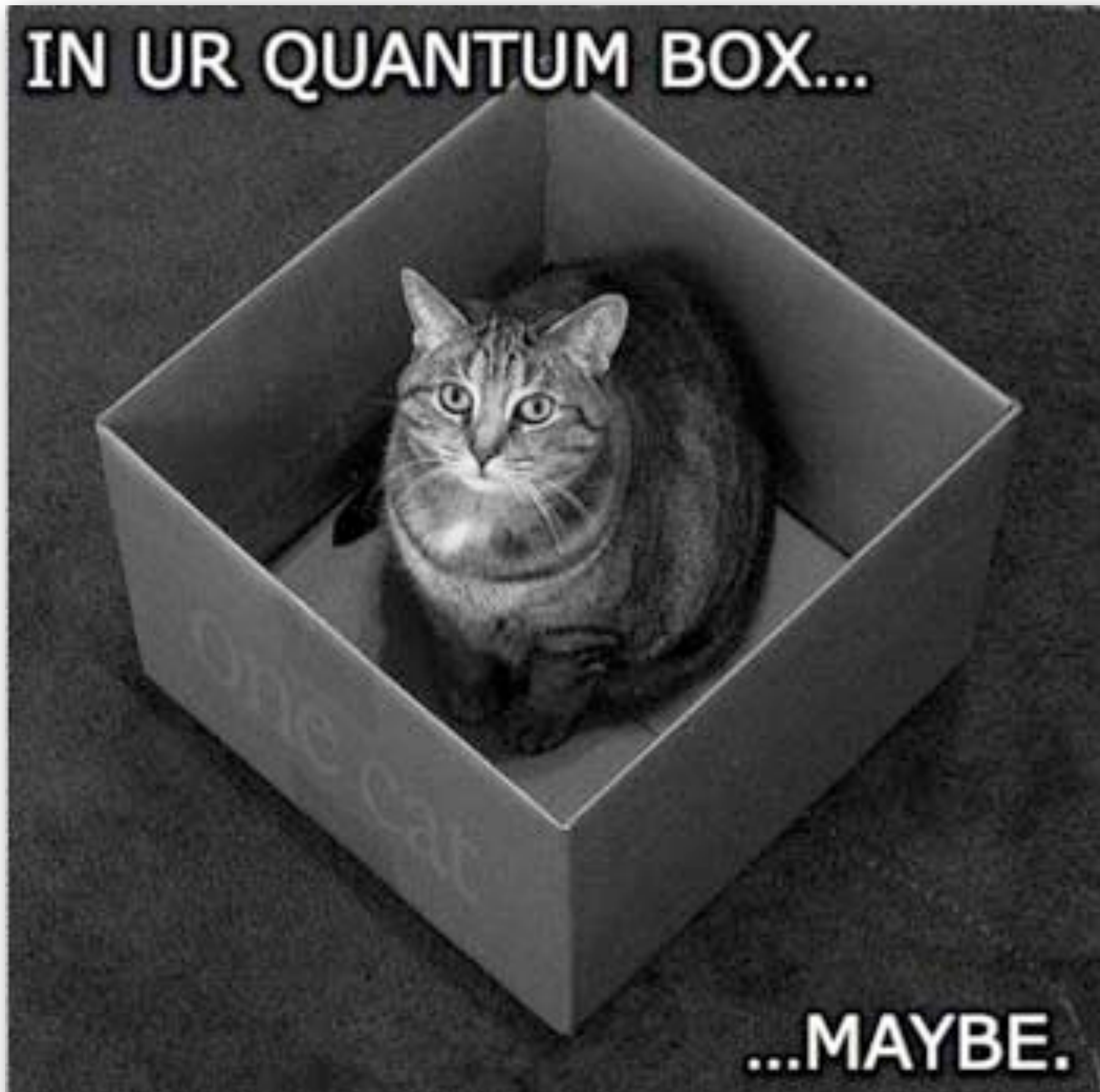
The Double-Slit Experiment

Dr Quantum explains the double-slit experiment.
From the film: *What the bleep do we know?*
See Lecture 1 video for full clip.

"Anyone who is not shocked by quantum theory has not understood it"

Niels Bohr

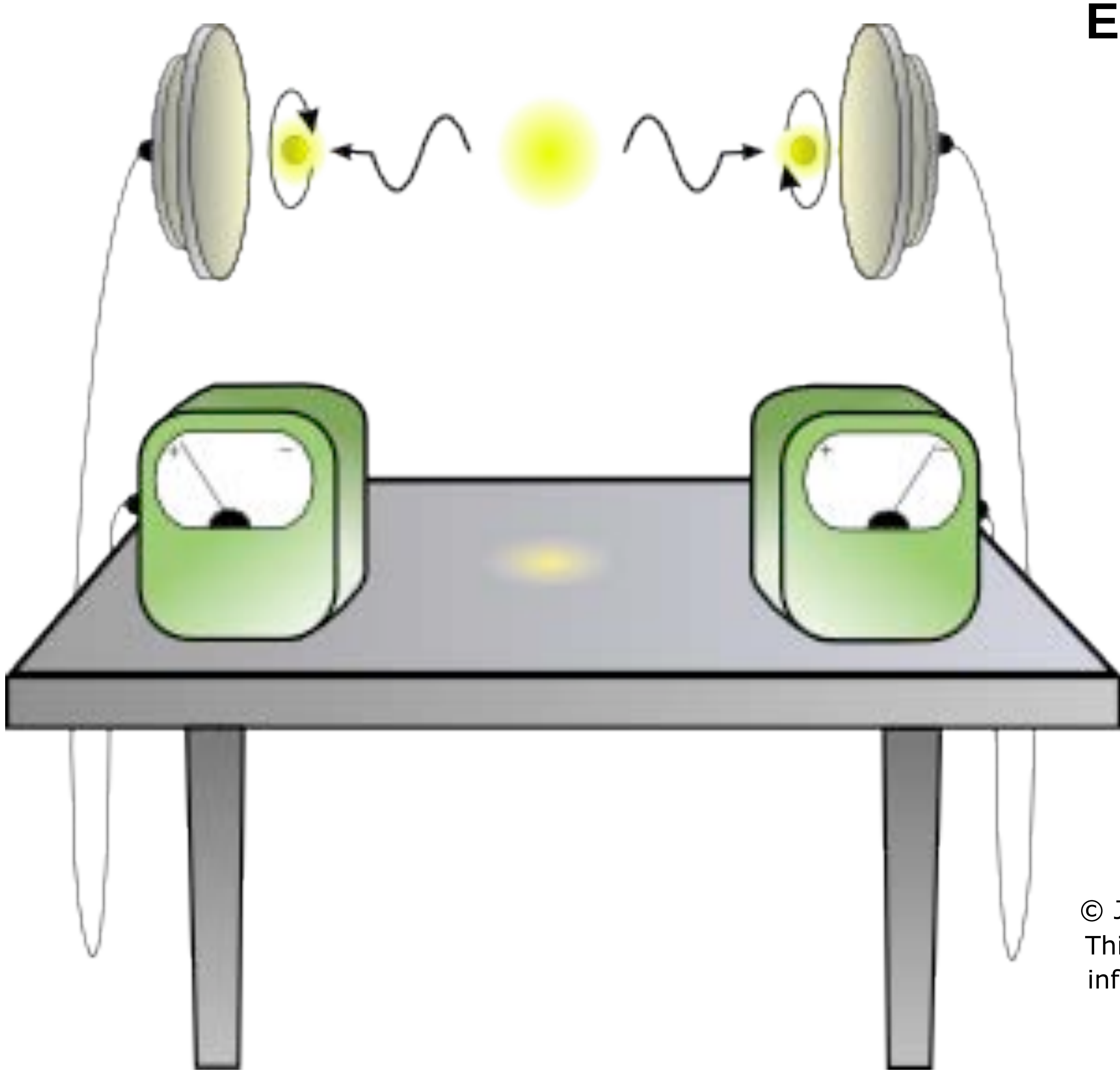
Schrödinger's Cat



Erwin Schrödinger
(1887 – 1961)

"I don't like it, and I'm sorry I ever had anything to do with it," Schrödinger, on the cat paradox.

EPR Paradox



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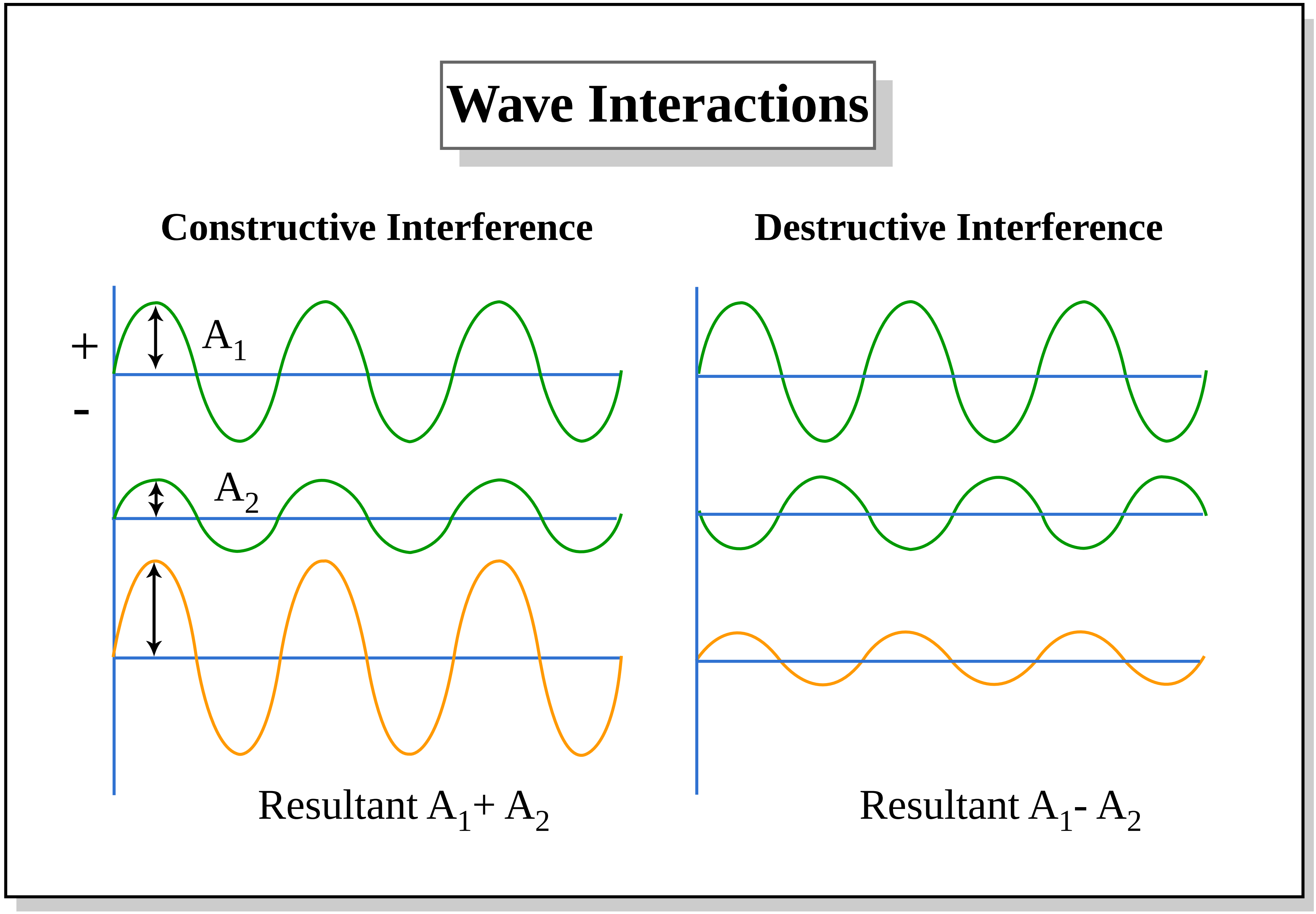
Einstein–Podolsky–Rosen

Wave-Particle Duality

- *Waves have particle-like properties:*
  - *Photoelectric effect: quanta (photons) are exchanged discretely*
  - *Energy spectrum of an incandescent body looks like a gas of very hot particles*

- Particles have wave-like properties:
  - Electrons in an atom are like standing waves (harmonics) in an organ pipe
  - Electrons beams can be diffracted, and we can see the fringes

Interference Patterns



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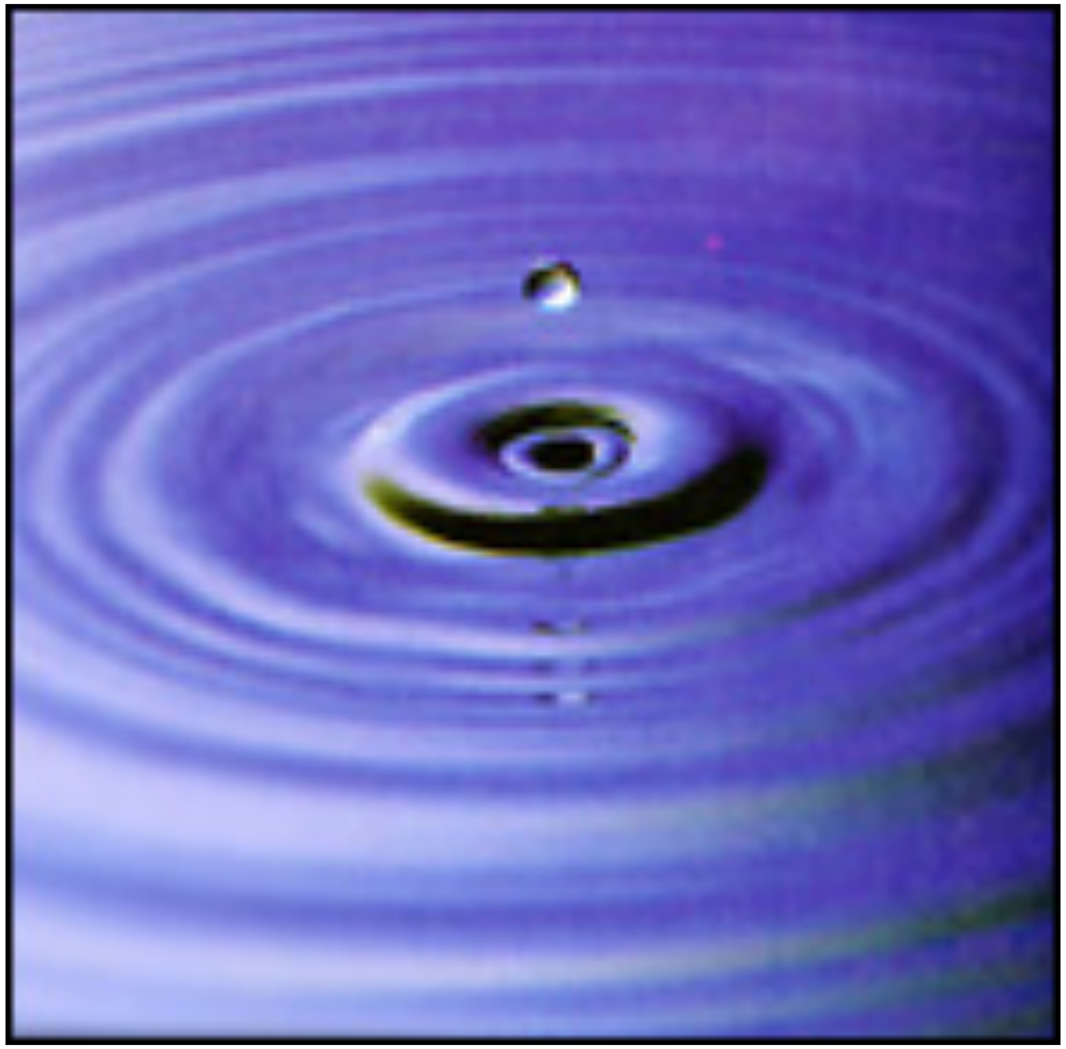
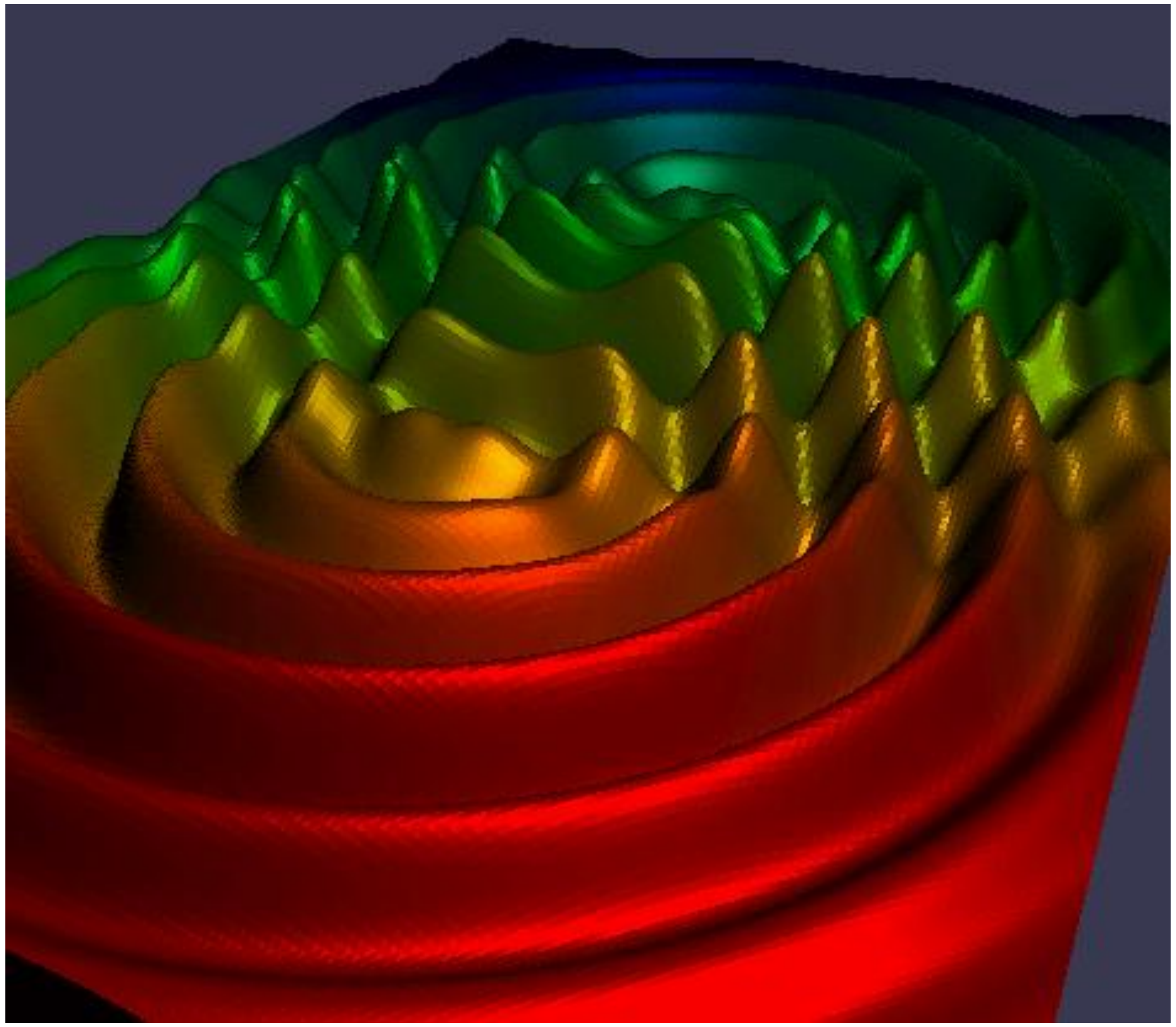
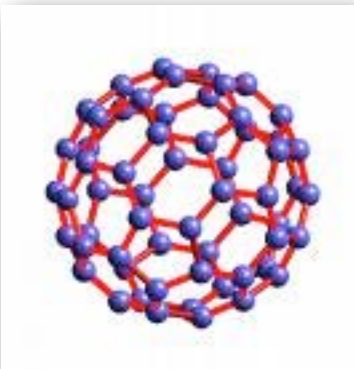
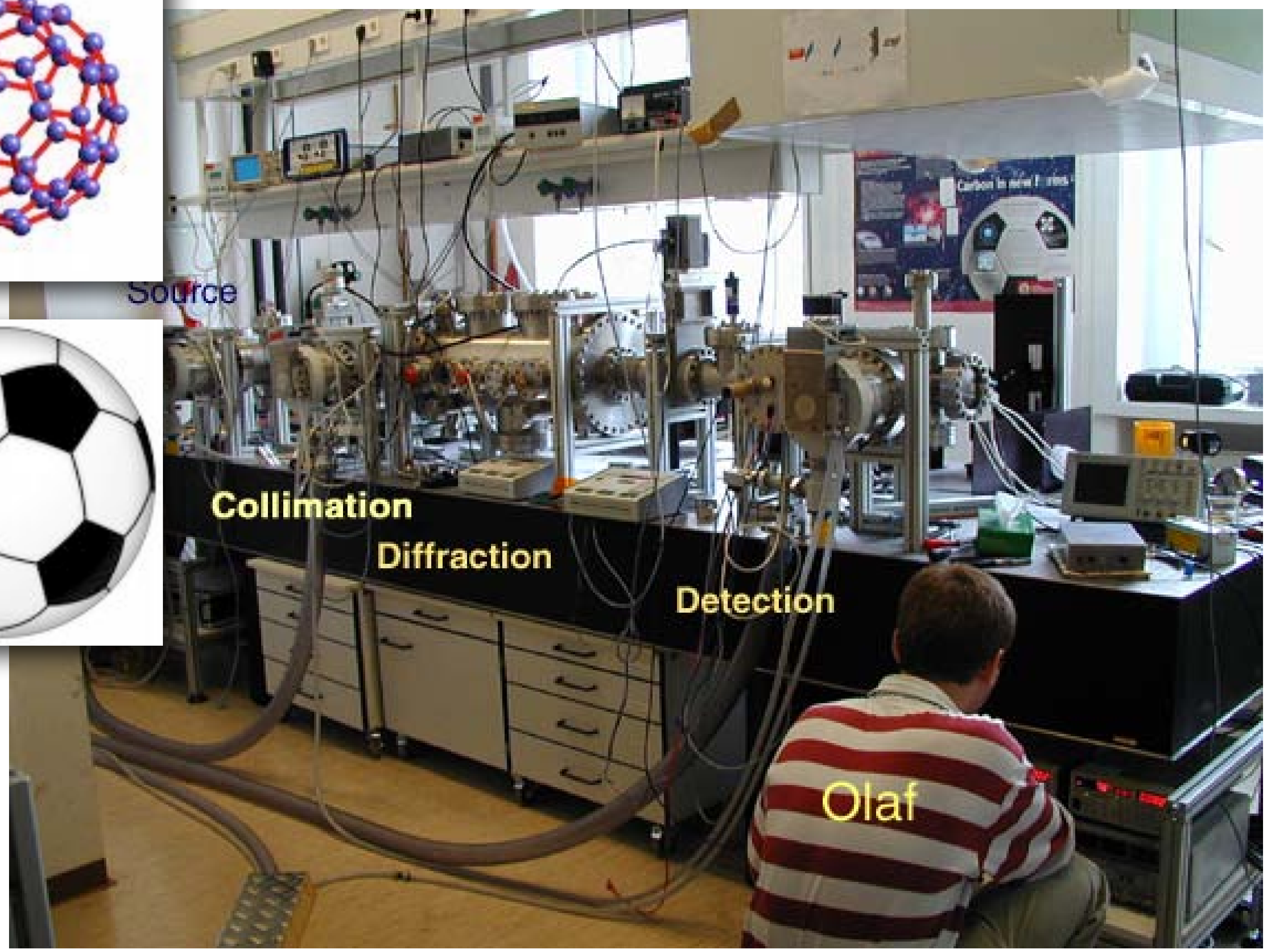
Interference Patterns

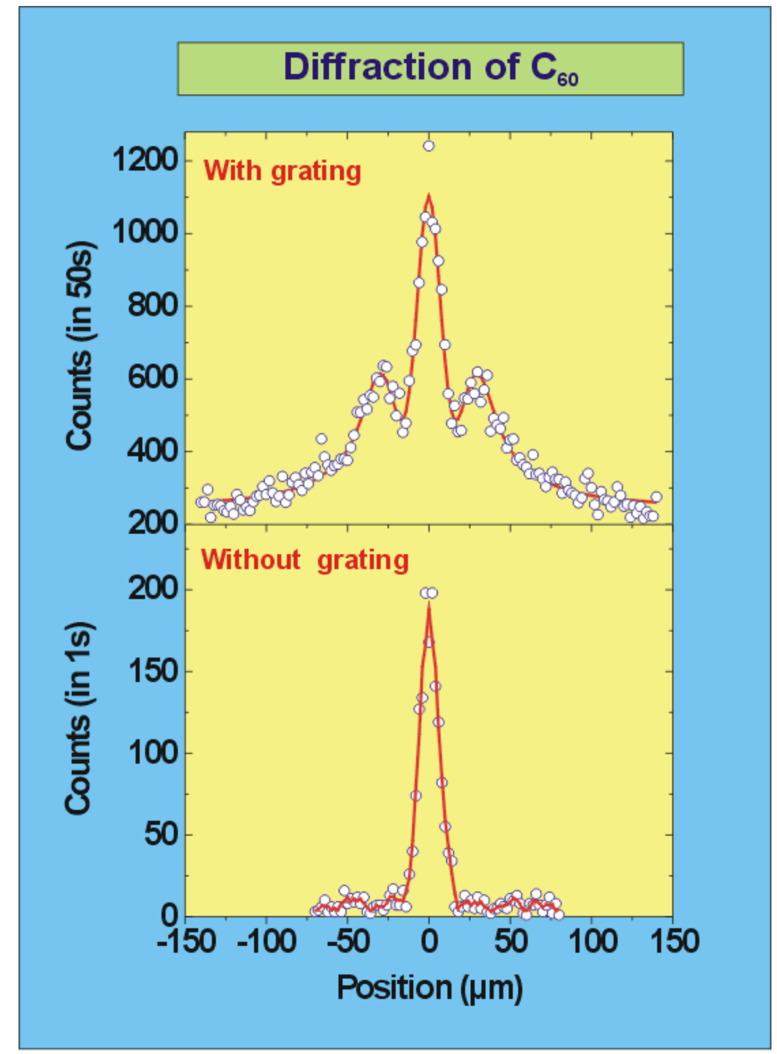




Bucky- and soccer balls







When is a particle like a wave?

Wavelengths:

Electron: 10^{-10} m
C60 Fullerene: 10^{-12} m
Baseball: 10^{-34} m
Human wavelength: 10^{-35} m

20 orders of magnitude smaller than the diameter of the nucleus of an atom!

Classical vs. quantum

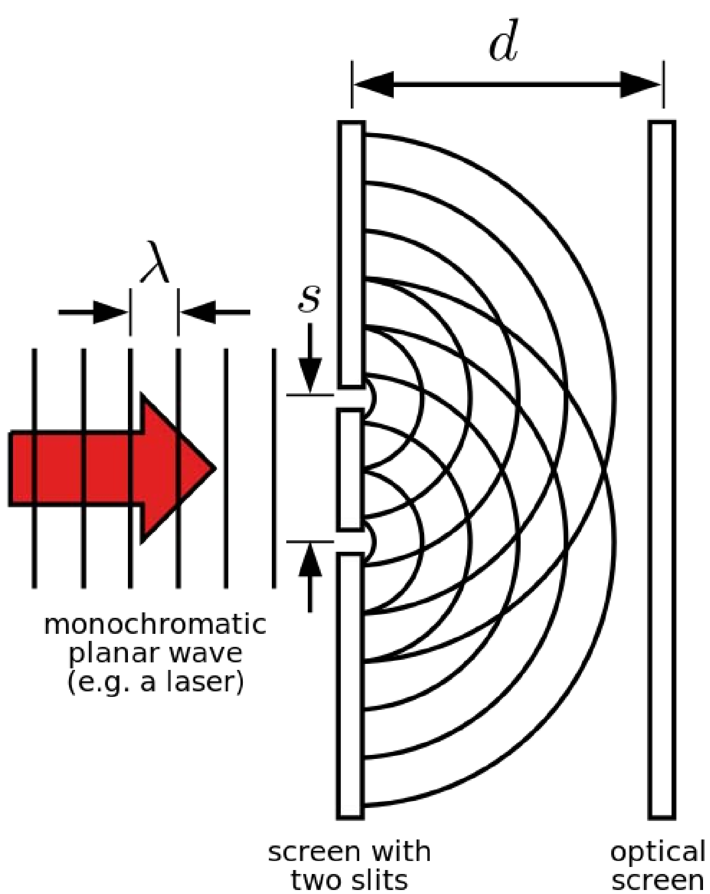
It is the mechanics of waves rather than classical particles.

Wave aspect of matter

light
matter

wave character

particle character



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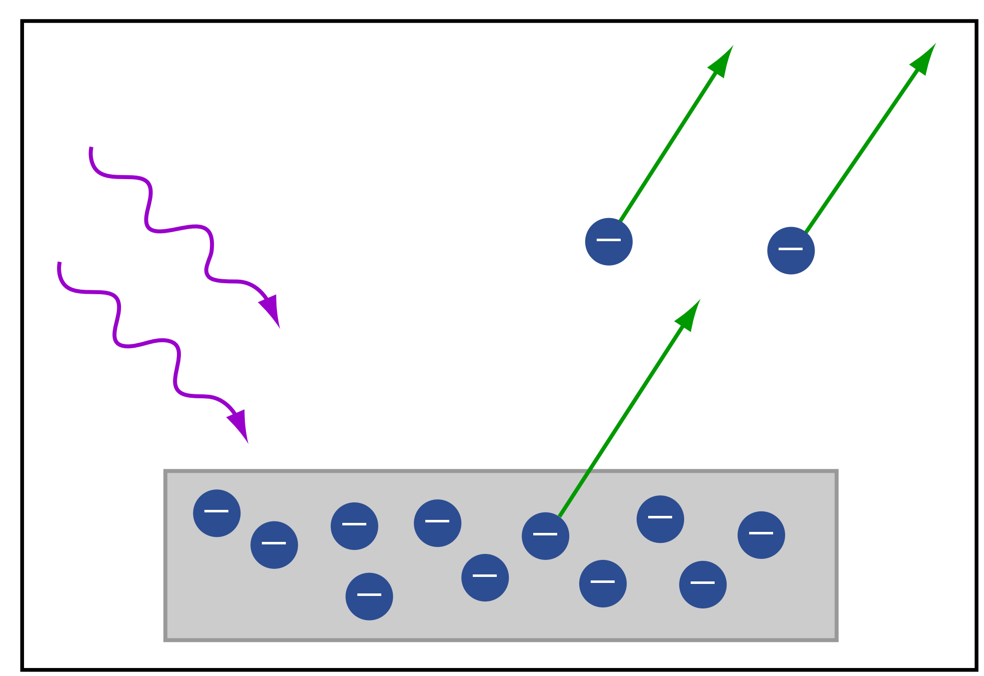

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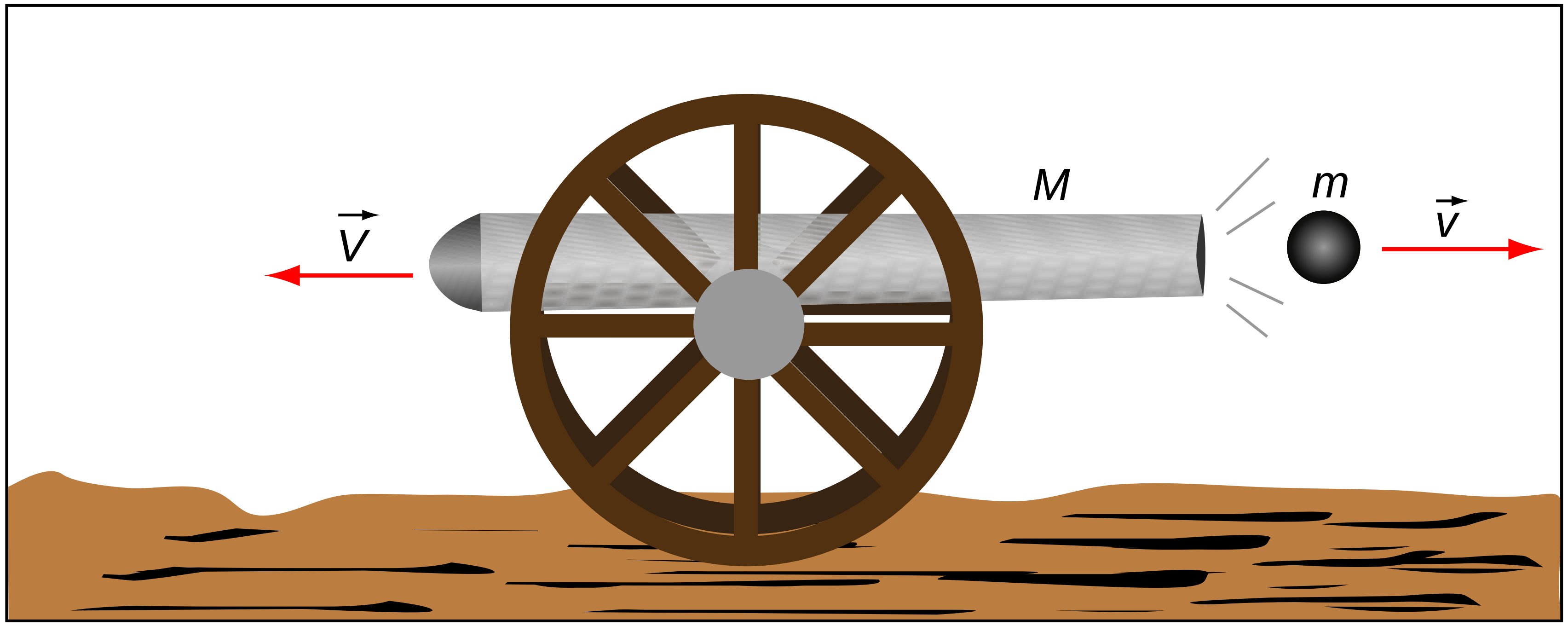
Mechanics of a Particle

$$m\frac{d^2\mathbf{r}}{dt^2} = F(\mathbf{r}) \longrightarrow \mathbf{r}(t)\ \ \mathbf{v}(t)$$

The sum of the kinetic and potential energy is conserved.



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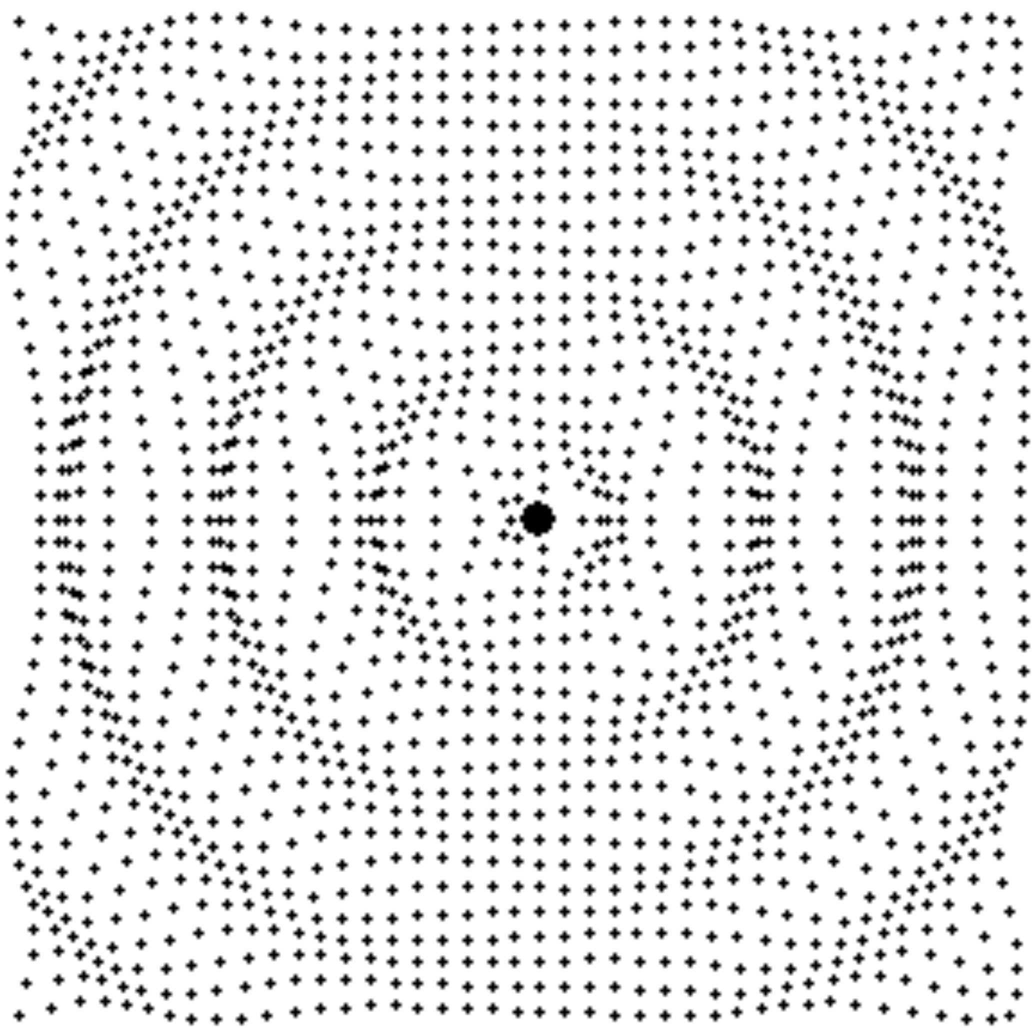
Description of a Wave



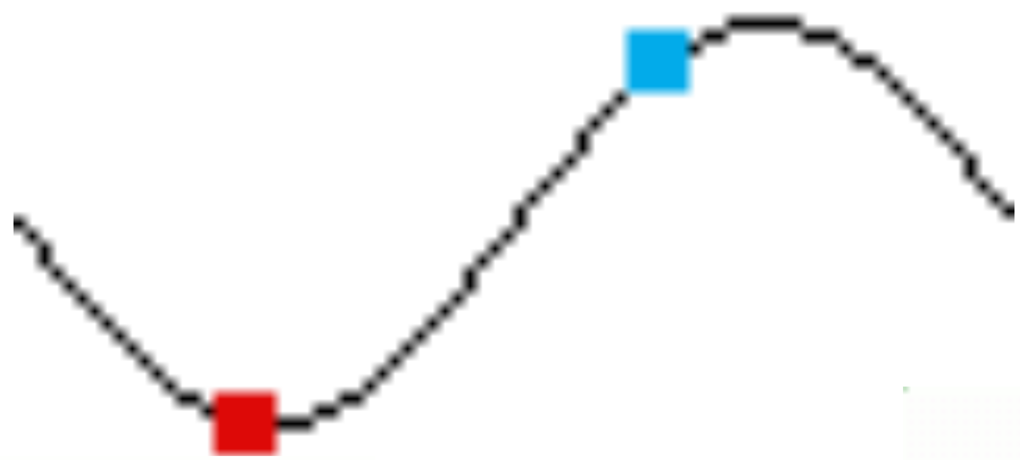
The wave is an excitation (a vibration): We need to know the amplitude of the excitation at every point and at every instant

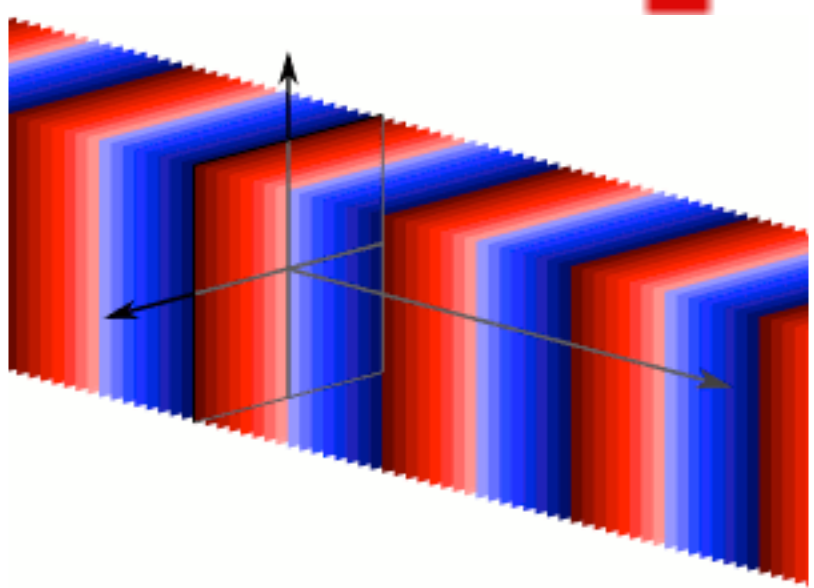
$$\Psi = \Psi(\mathbf{r}, t)$$

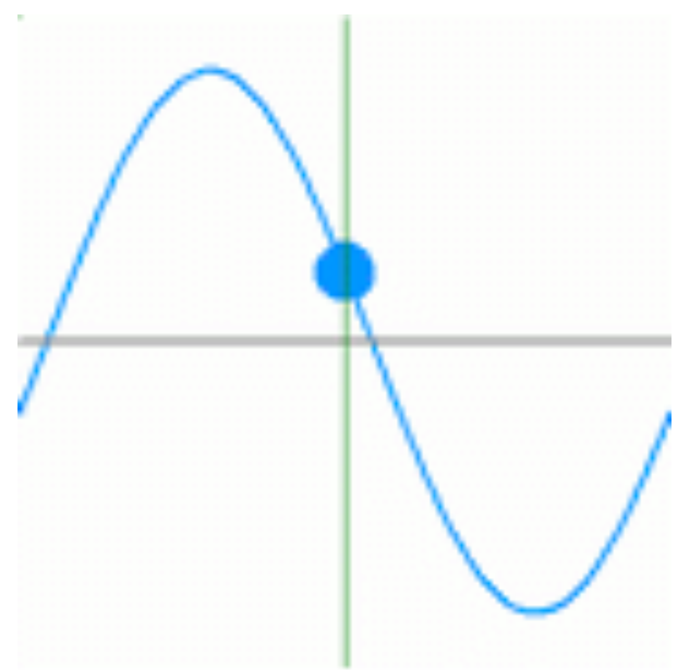
Mechanics of a Wave

Free particle, with an assigned momentum:

$$\Psi(\mathbf{r},t) = A\exp[i(\mathbf{k}\bullet\mathbf{r} - \omega t)]$$







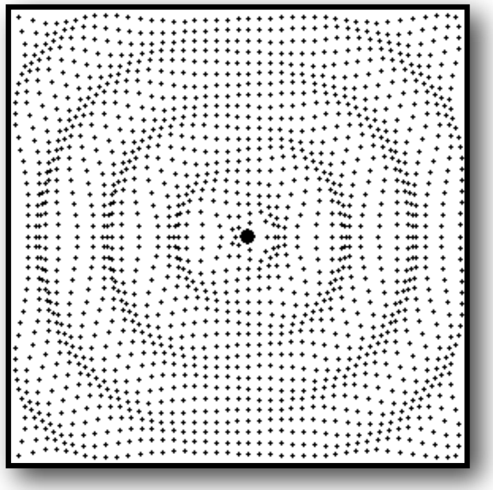
Wave aspect of matter

particle: E and momentum $\vec{p}$

wave: frequency ν and wavevector $\vec{k}$

$$E = h\nu = \hbar\omega$$

$$\vec{p} = \hbar\vec{k} = \frac{h}{\lambda}\frac{\vec{k}}{|\vec{k}|}$$



de Broglie: free particle can be described as planewave $\psi(\vec{r},t) = Ae^{i(\vec{k}\cdot\vec{r}-\omega t)}$ with $\lambda = \dfrac{h}{mv}$

How do we describe the physical behavior of particles as waves?

The Schrödinger equation

a wave equation:

second derivative in space
first derivative in time

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right]\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)$$

Hamiltonian

$$\begin{aligned} H &= -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t) = \\ &= \frac{p^2}{2m} + V = T + V \end{aligned}$$

$$\vec{p} = -i\hbar\nabla$$

In practice ...

H time independent: $\psi(\vec{r},t) = \psi(\vec{r}) \cdot f(t)$

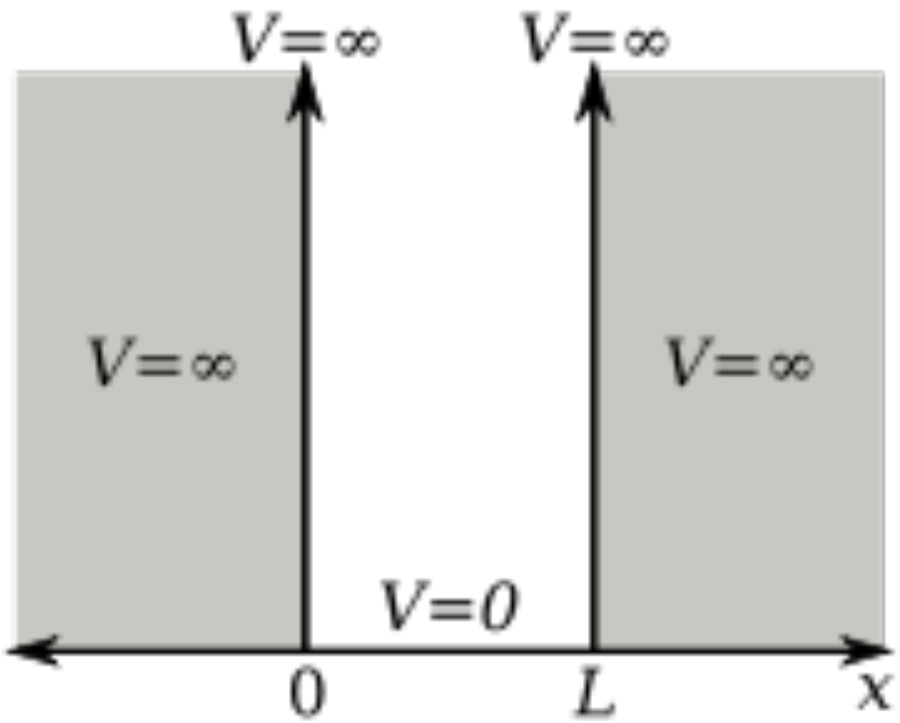
$$i\hbar \frac{\dot{f}(t)}{f(t)} = \frac{H\psi(\vec{r})}{\psi(\vec{r})} = \text{const.} = E$$

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

$$\psi(\vec{r},t) = \psi(\vec{r}) \cdot e^{-\frac{i}{\hbar}Et}$$

time independent Schrödinger equation
stationary Schrödinger equation

Particle in a box



Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (1)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad (2)$$

boundary conditions

$$\psi(0) = \psi(L) = 0 \quad (4)$$

$$\psi(x) = A\sin(kx) \quad (5)$$

$$\psi(L) = A\sin(kL) = 0 \quad (6)$$

general solution

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

$$E = \frac{k^2\hbar^2}{2m} \quad (3)$$

Boundary conditions cause quantization!

Particle in a box

quantization

$$k = \frac{n\pi}{L} \quad \text{where} \quad n \in \mathbb{Z}^+ \qquad (7)$$

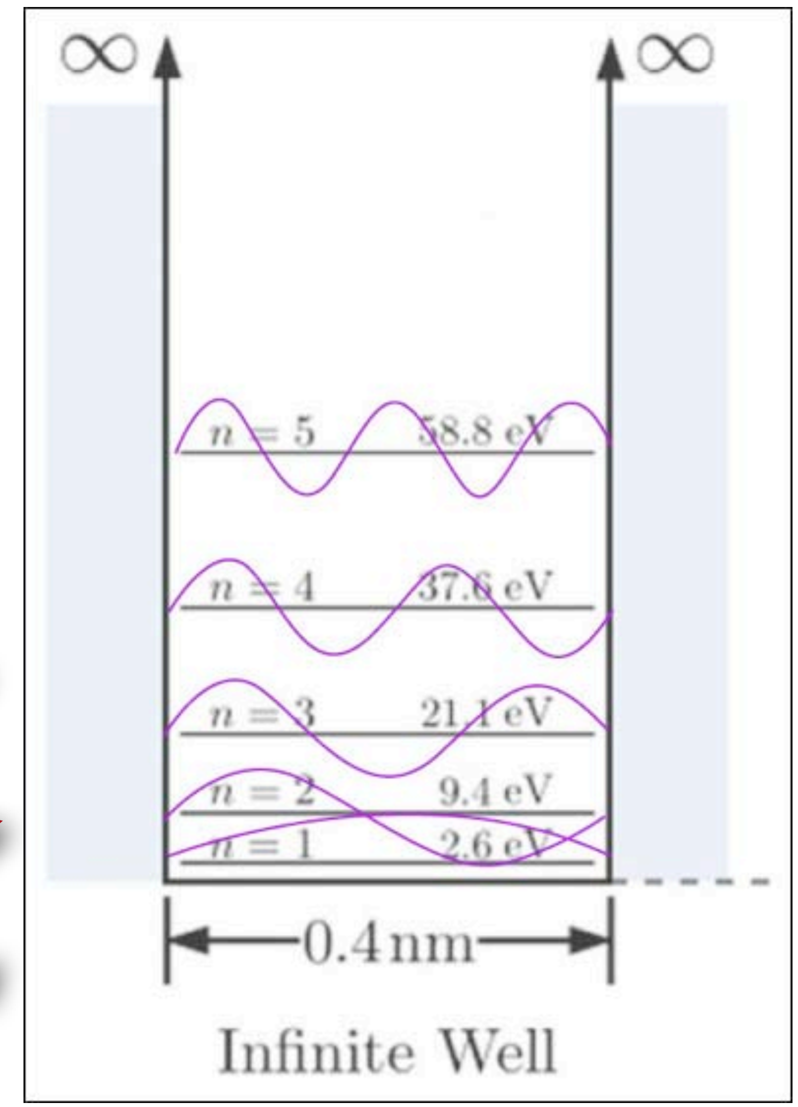
normalization

$$1 = \int_{-\infty}^{\infty} |\psi(x)|^2 \, \mathrm{d}x = |A|^2 \int_0^L \sin^2(kx) \, \mathrm{d}x = |A|^2 \frac{L}{2}$$

solution

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad (9)$$

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \qquad (10)$$



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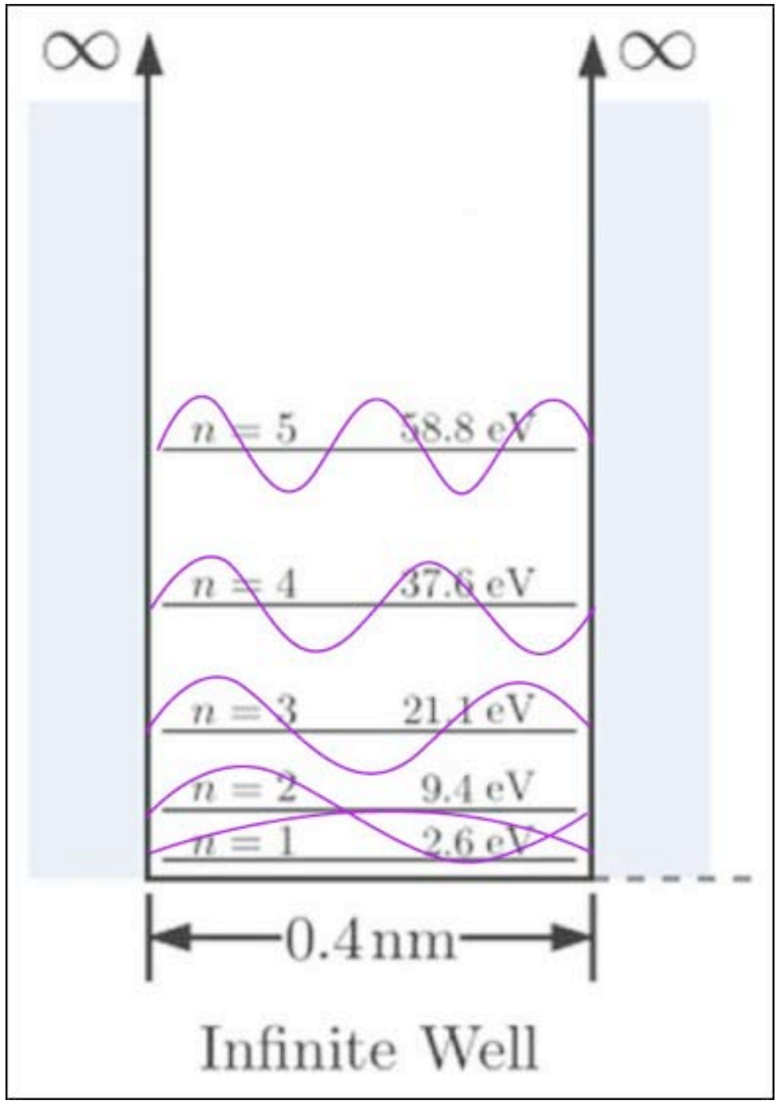
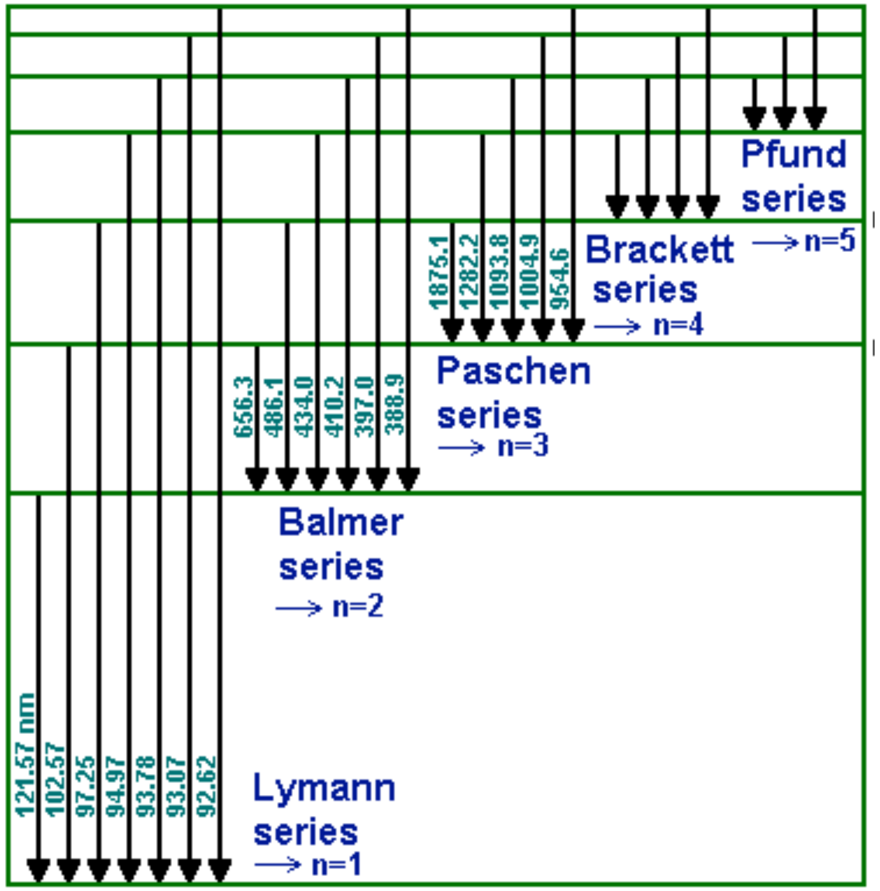
quantum number

Simple examples

electron in square well



electron in hydrogen atom



Harmonic oscillator

$$V(x) = \frac{1}{2}m\omega^2 x^2$$

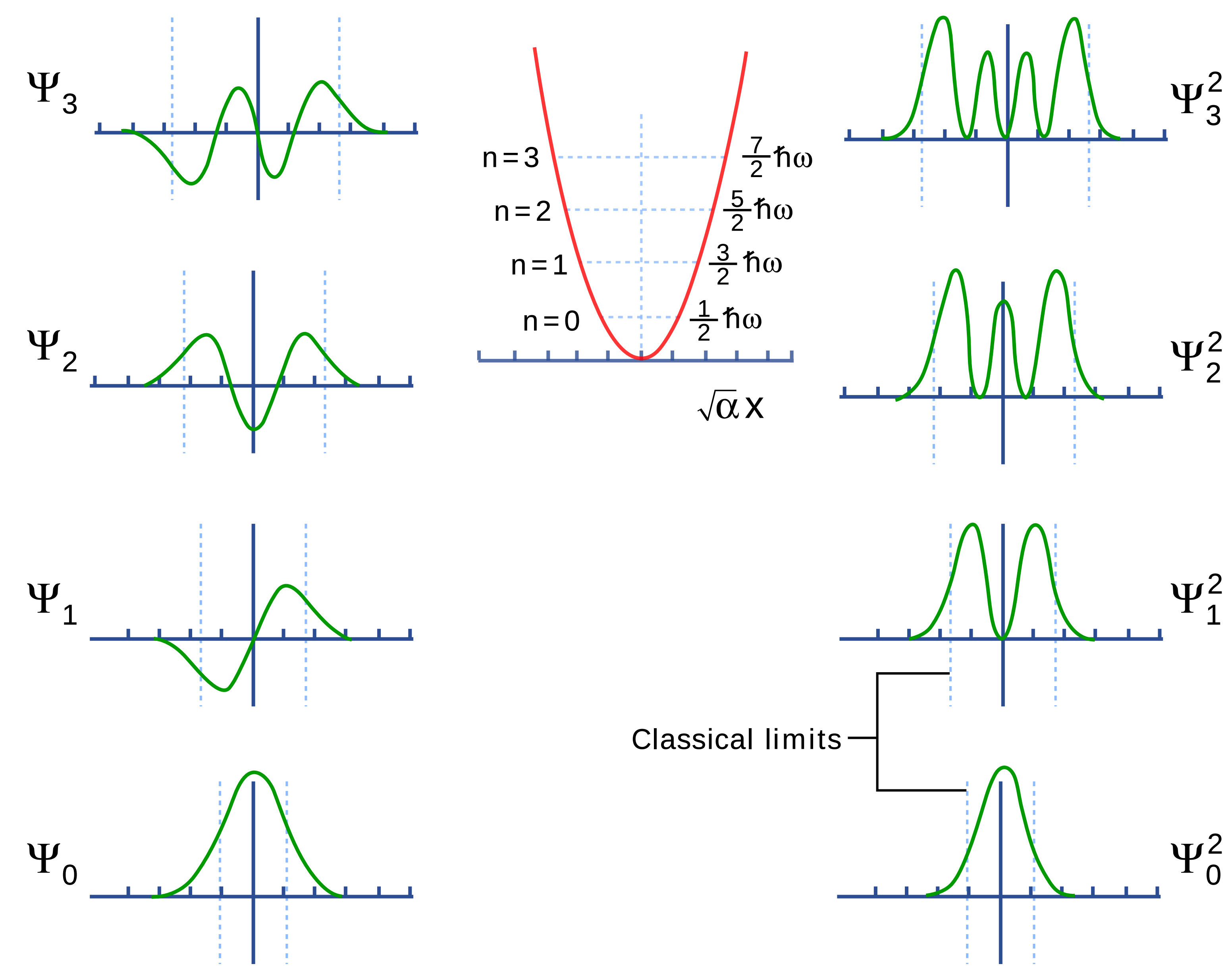
$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

solve Schrödinger equation

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$\langle x|\psi_n\rangle = \sqrt{\frac{1}{2^n\, n!}} \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \cdot \exp\left(-\frac{m\omega x^2}{2\hbar}\right) \cdot H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$$

Harmonic oscillator



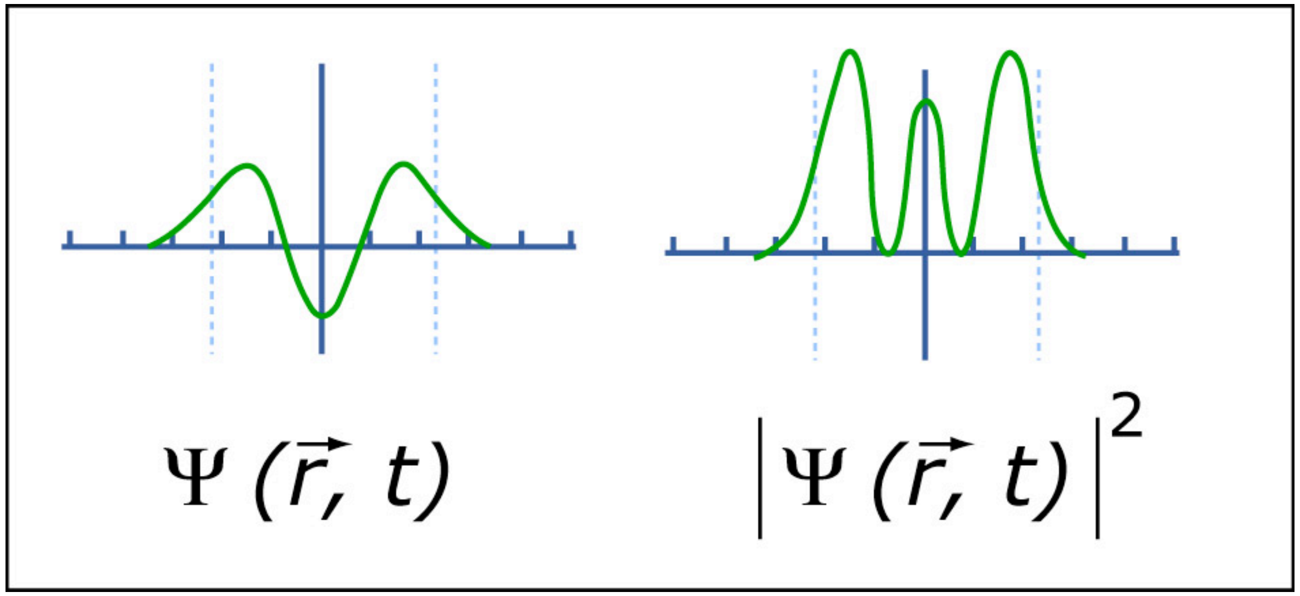
Graphs of the quantum harmonic oscillator potential and wavefunctions.

Image by MIT OpenCourseWare.

Interpretation of a wavefunction

$\psi(\vec{r}, t)$ → wave function (complex)

$|\psi|^2 = \psi\psi^*$ → interpretation as probability to find particle (that is, if a measurement is made)



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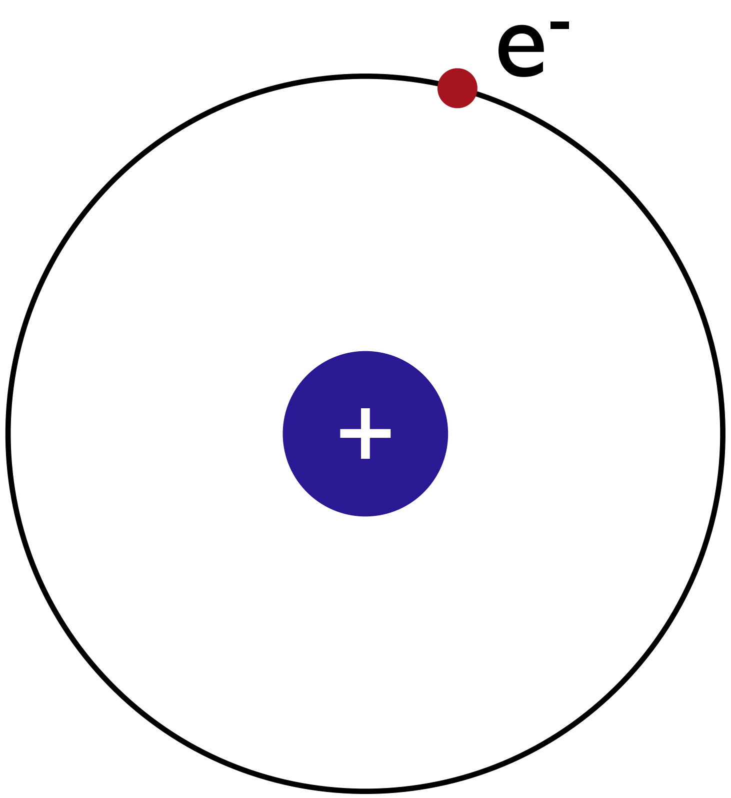
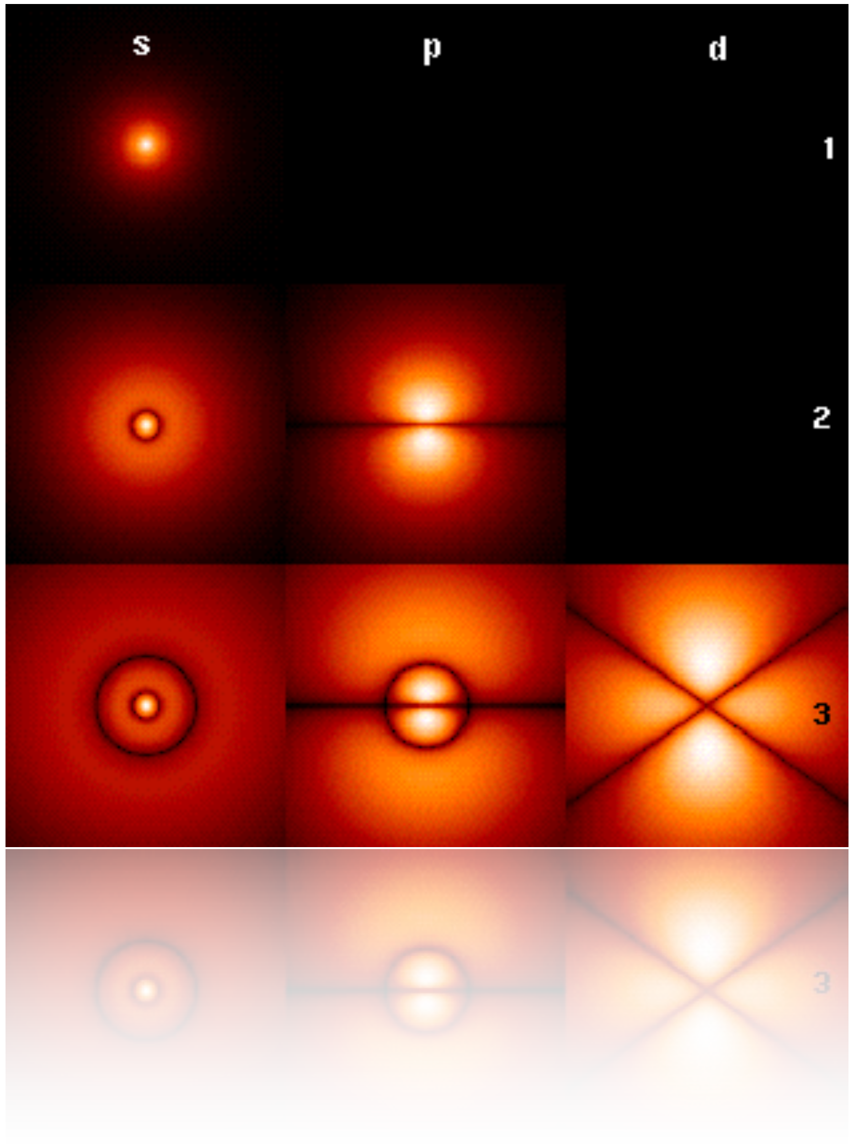
$$\int_{-\infty}^{\infty} \psi\psi^* dV = 1$$

Connection to reality?

potential: 1/r



hydrogen atom



Many Interpretations of Quantum Mechanics!

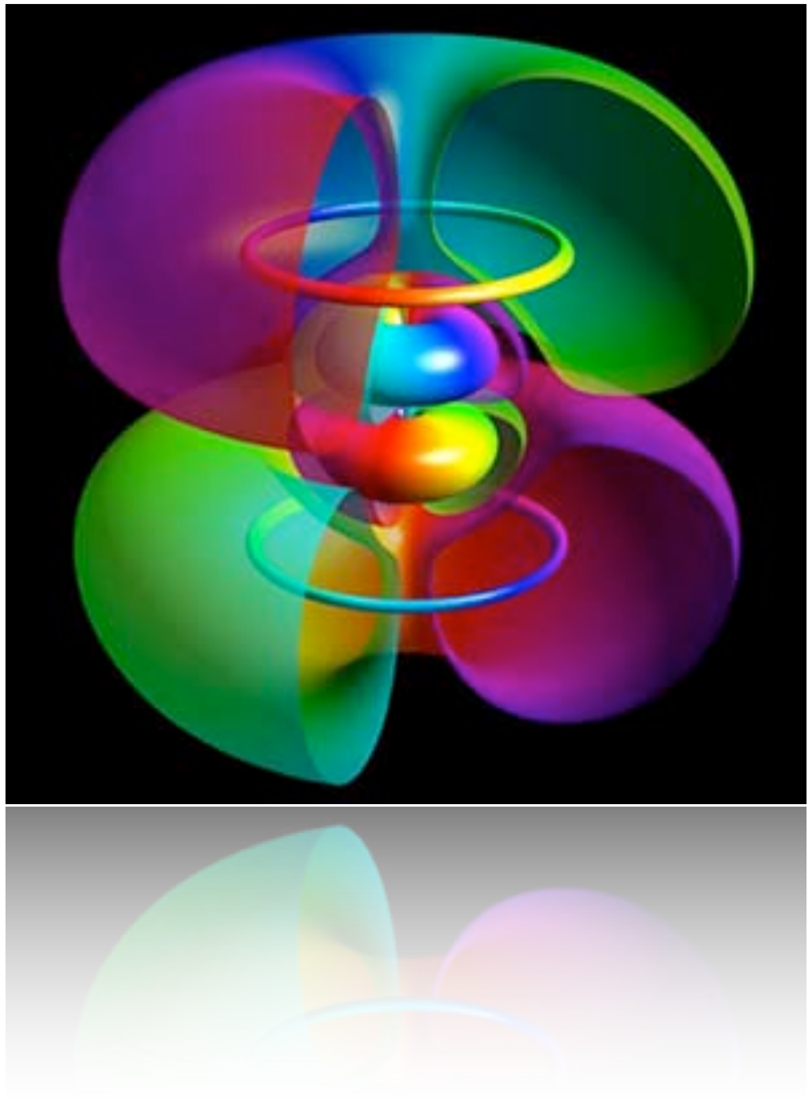
Interpretation	Author(s)	Deterministic?	Wavefunction real?	Unique history?	Hidden variables?	Collapsing wavefunctions?	Observer role?
Ensemble interpretation	Max Born, 1926	No	No	Yes	Agnostic	No	None
Copenhagen interpretation	Niels Bohr, Werner Heisenberg, 1927	No	No	Yes	No	NA	NA
Hydrodynamic interpretation	Erwin Madelung, 1927	Yes	Yes	Yes	No	No	None
de Broglie-Bohm theory	Louis de Broglie, 1927, David Bohm, 1952	Yes	Yes[5]	Yes[6]	Yes	No	None
von Neumann interpretation	John von Neumann, 1932	No	Yes	Yes	No	Yes	Causal
Quantum logic	Garrett Birkhoff, 1936	Agnostic	Agnostic	Yes[3]	No	No	Interpretational[2]
Many-worlds interpretation	Hugh Everett, 1957	Yes	Yes	No	No	No	None
Stochastic mechanics	Edward Nelson, 1966	No	No	Yes	No	No	None
Many-minds interpretation	H. Dieter Zeh, 1970	Yes	Yes	No	No	No	Interpretational[4]
Consistent histories	Robert B. Griffiths, 1984	Agnostic[1]	Agnostic[1]	No	No	No	Interpretational[2]
Objective collapse theories	Ghirardi-Rimini-Weber, 1986	No	Yes	Yes	No	Yes	None
Transactional interpretation	John G. Cramer, 1986	No	Yes	Yes	No	Yes[7]	None
Relational interpretation	Carlo Rovelli, 1994	No	Yes	Agnostic[8]	No	Yes[9]	Intrinsic[10]
Incomplete measurements	Christophe de Dinechin, 2006	No	No[11]	Yes	No	Yes[11]	Interpretational[2]

Source: Wikipedia

Summary

Review

- Why quantum mechanics?
- Wave aspect of matter
- Interpretation
- The Schrödinger equation
- Simple examples



Literature

- Greiner, Quantum Mechanics: An Introduction
- Thaller, Visual Quantum Mechanics
- Feynman, The Feynman Lectures on Physics
- wikipedia, "quantum mechanics", "Hamiltonian operator", "Schrödinger equation", ...