1.021, 3.021, 10.333, 22.00 : Introduction to Modeling and Simulation : Spring 2011

Part II – Quantum Mechanical Methods : Lecture 1

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

Jeffrey C. Grossman

Department of Materials Science and Engineering
Massachusetts Institute of Technology

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

1. It's A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. The Many-Body Problem: From Many-Body to Single-Particle
4. Quantum modeling of materials
5. From Atoms to Solids
6. Basic properties of materials
7. Advanced properties of materials
8. What else can we do?

Part II Outline

theory & practice

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. From Atoms to Solids
5. Quantum Modeling of Solids: Basic Properties
6. Advanced Prop. of Materials: What else can we do?

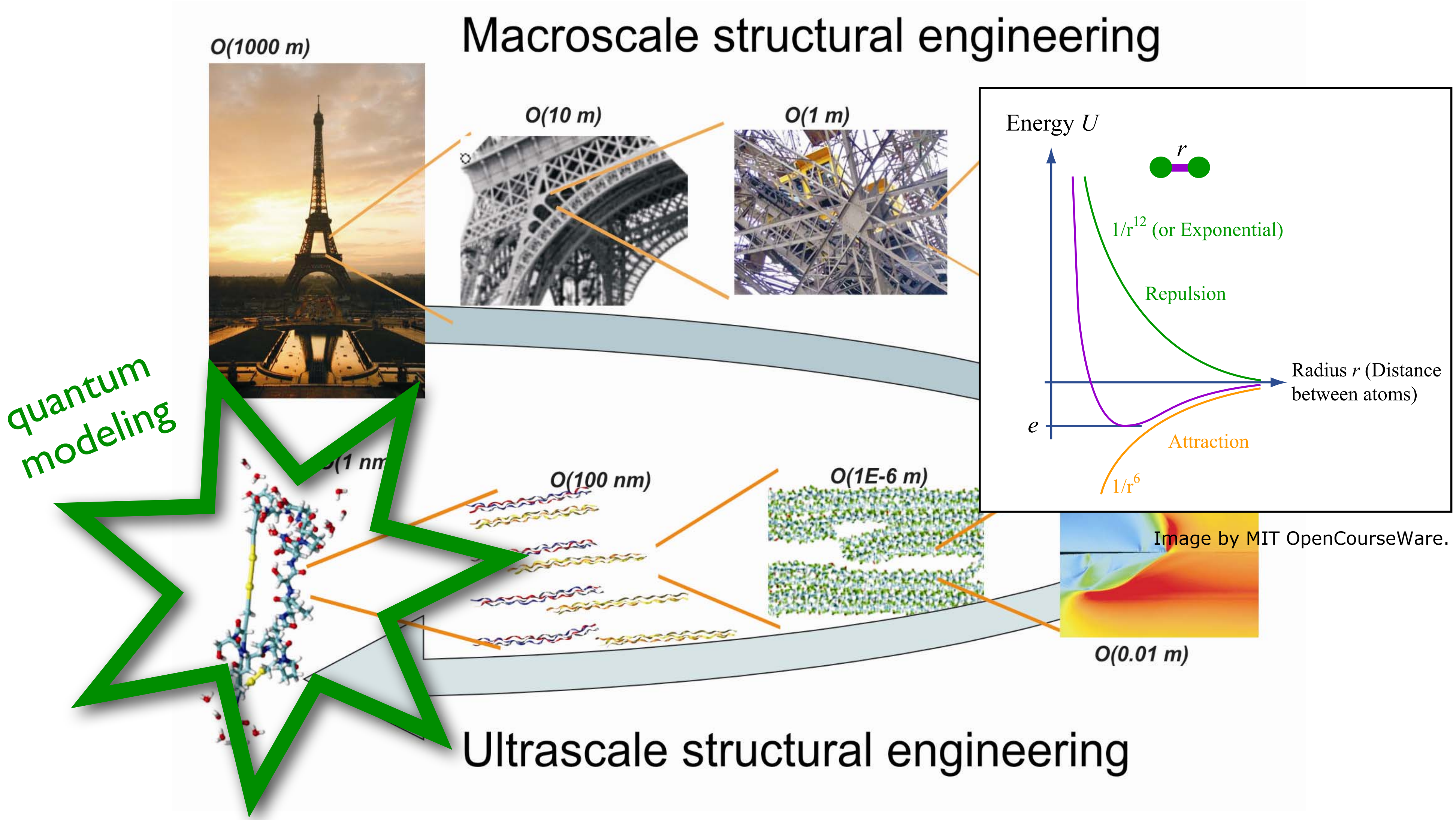
example applications

7. Nanotechnology
8. Solar Photovoltaics: Converting Photons into Electrons
9. Thermoelectrics: Converting Heat into Electricity
10. Solar Fuels: Pushing Electrons up a Hill
11. Hydrogen Storage: the Strength of Weak Interactions
12. Review

Lesson outline

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

Multi-scale modeling



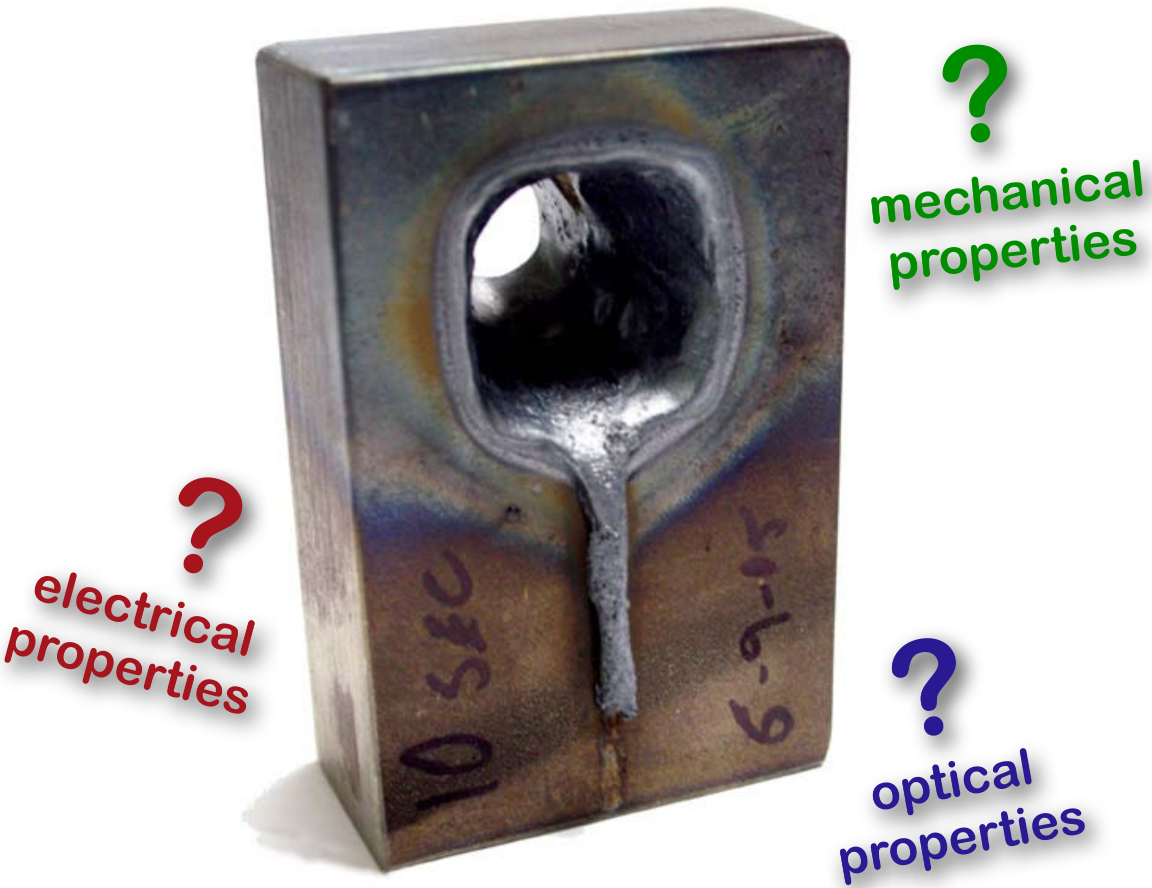
It’s a quantum world!

Image of invisibility cloak removed due to copyright restrictions. Please see
http://www.sciencenews.org/view/generic/id/69415/title/Invisibility_cloaks_hit_the_big_time.

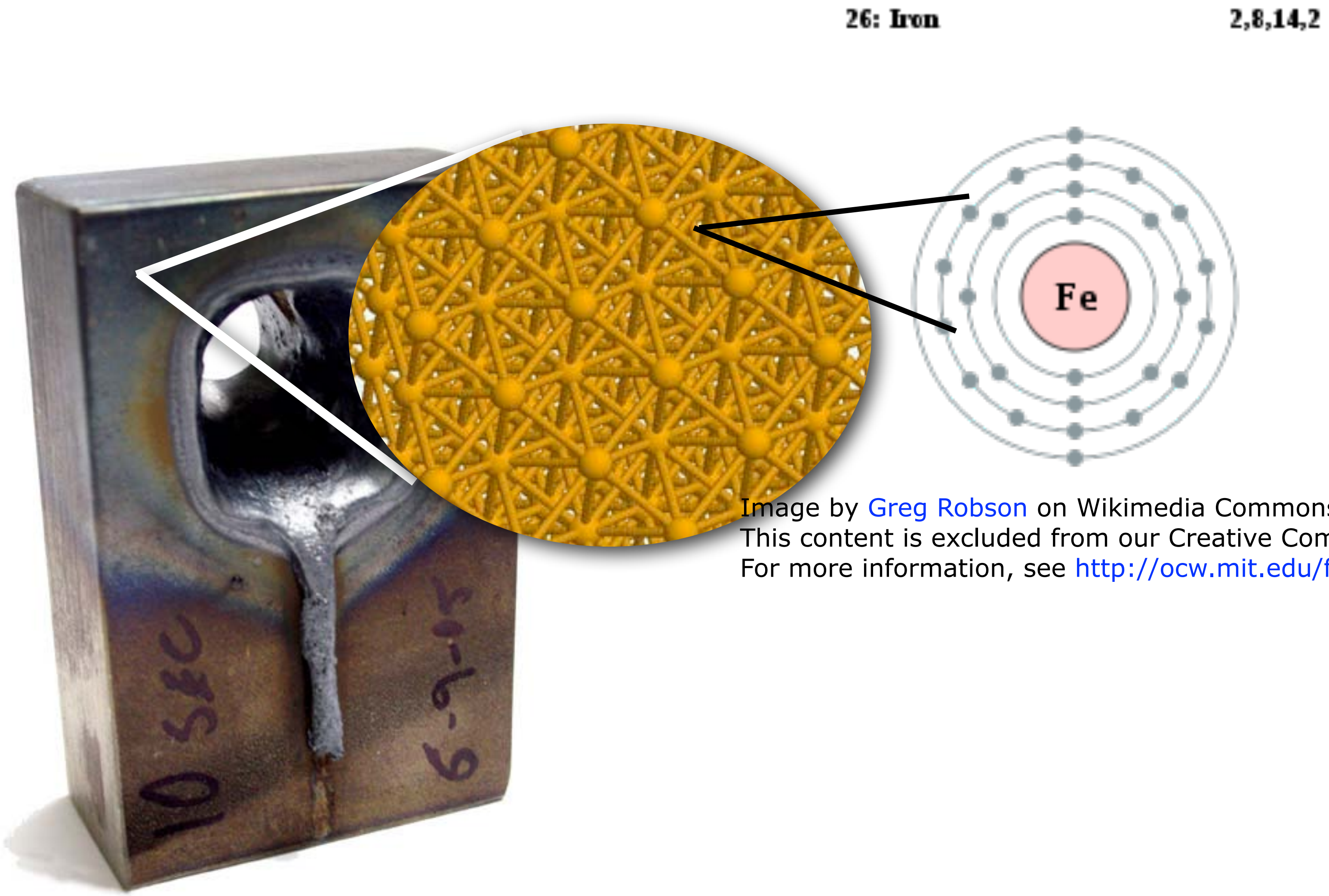
Motivation

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

Quantum modeling/ simulation



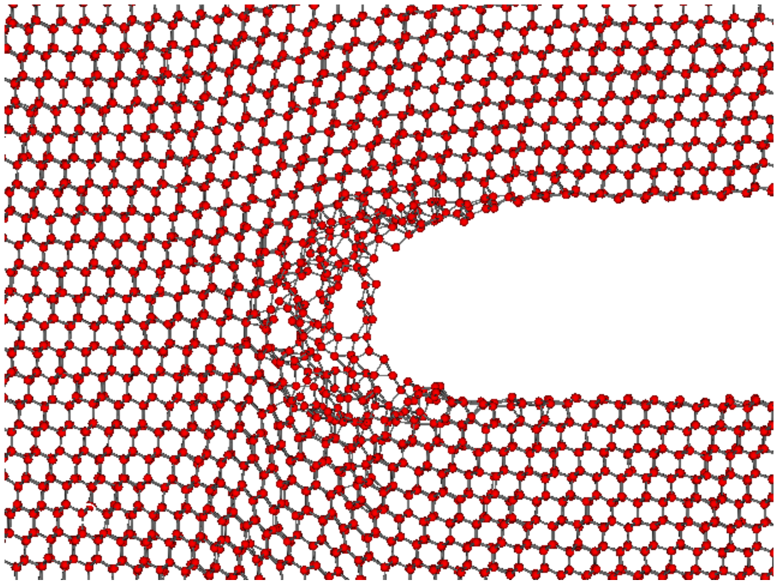
A simple iron atom ...



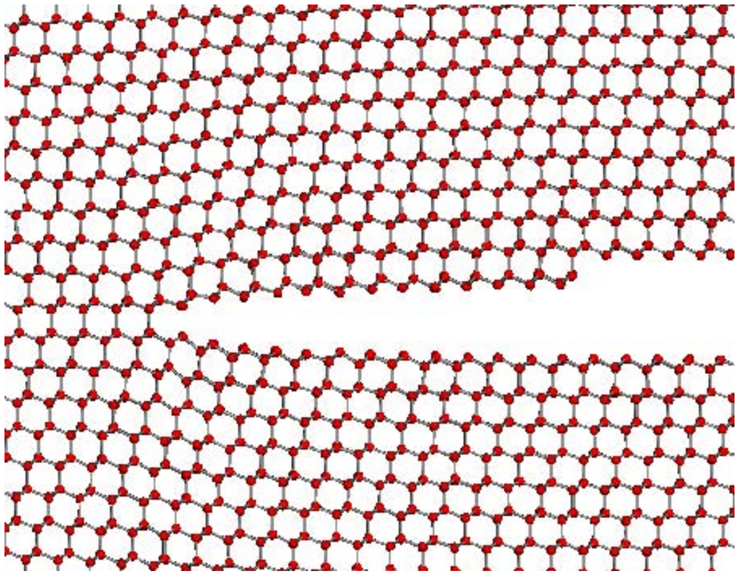
Why Quantum Mechanics?

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

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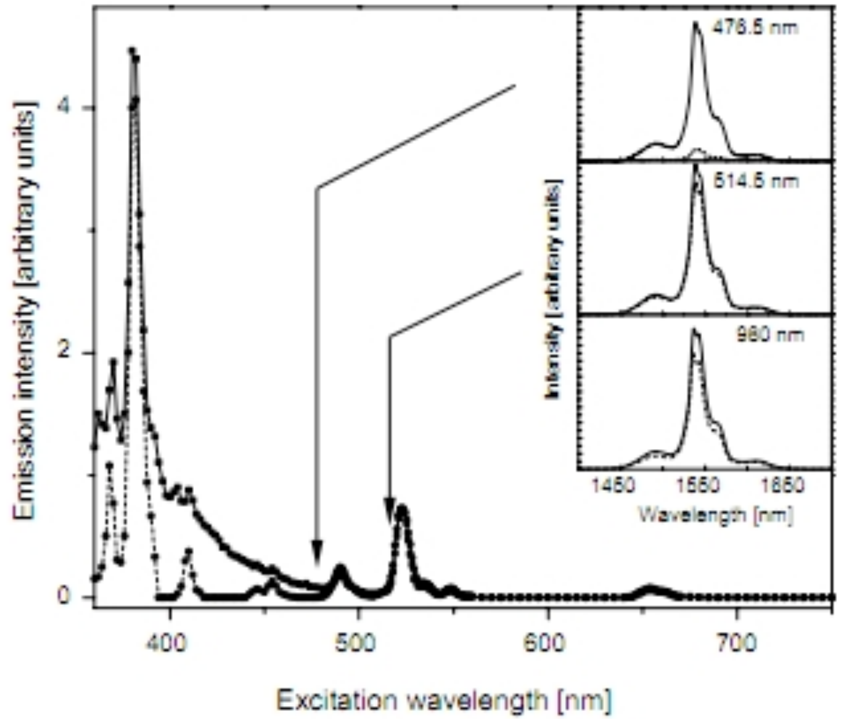
Please see Vangberg, T. R. Lie, and A. Ghosh.
"Symmetry-Breaking Phenomena in Metalloporphyrn in Pi-Cation Radicals."

Jahn-Teller effect in porphyrins (A. Ghosh)



Non-resonant Raman in silicates (Lazzeri and Mauri)

Reactions

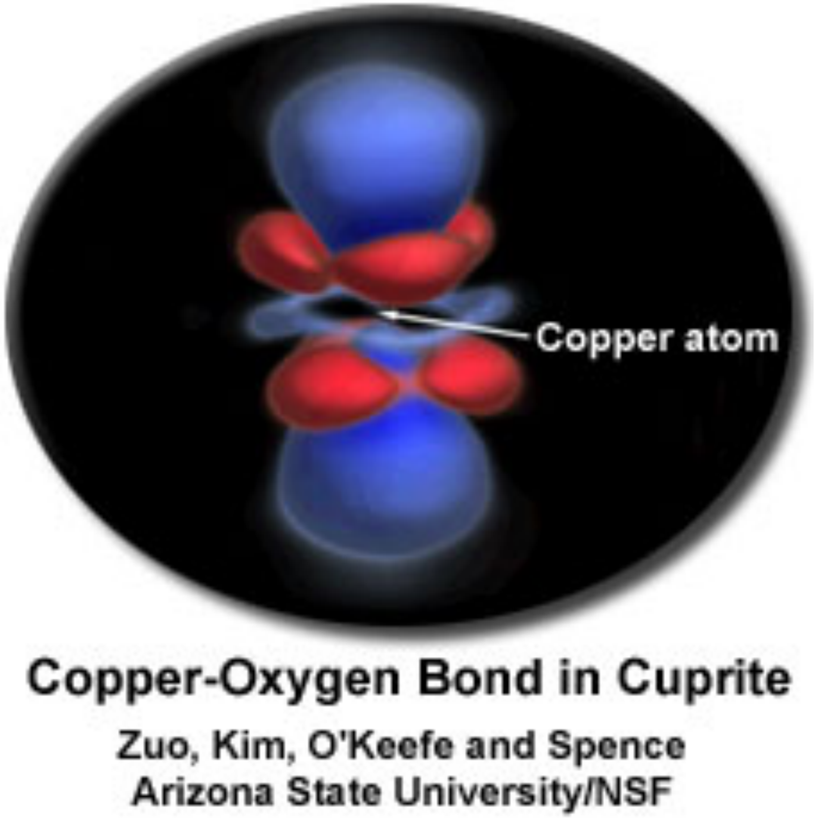
Chemical reaction image removed due to copyright restrictions.

1,3-butadiene + ethylene → cyclohexene

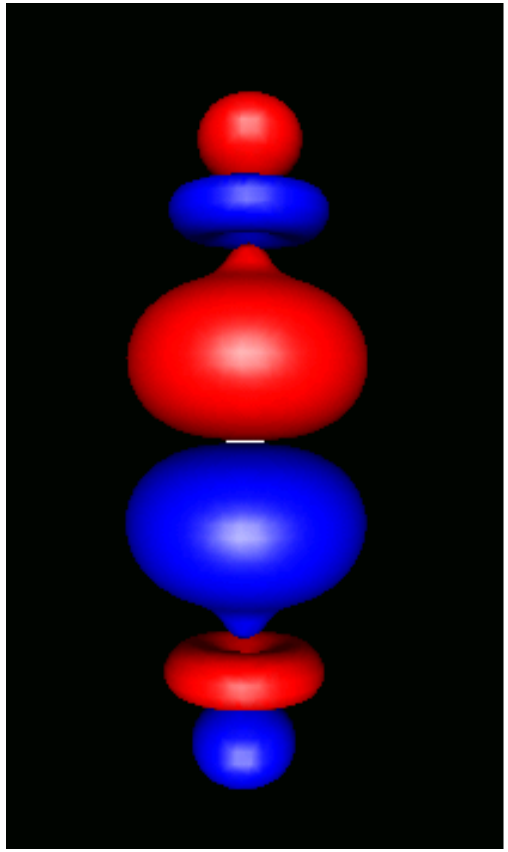
Standard Model of Matter

- 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?

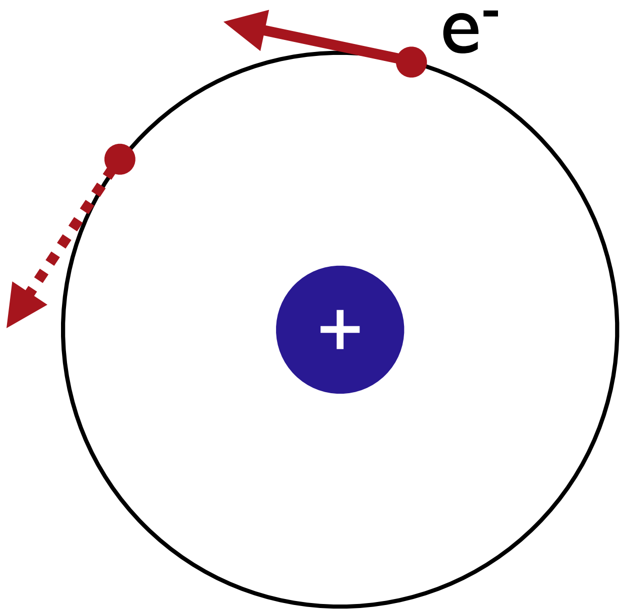
Problems in classical physics that
led to quantum mechanics:

- “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”

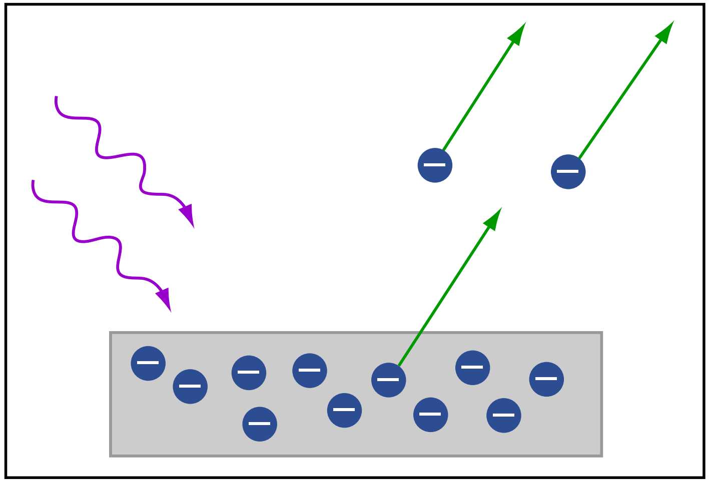


hydrogen atom

problem:
accelerated charge causes radiation, atom not stable!

Quantization of properties

photoelectric effect



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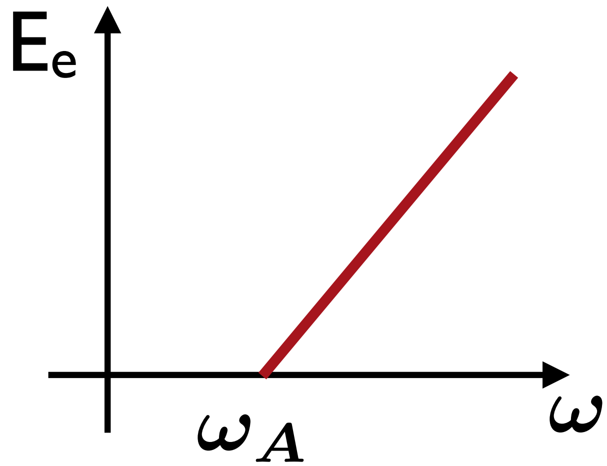


$$E = \hbar(\omega - \omega_A) = h(\nu - \nu_A)$$

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

Einstein: photon $E = \hbar\omega$

Quantization of properties

atomic spectra

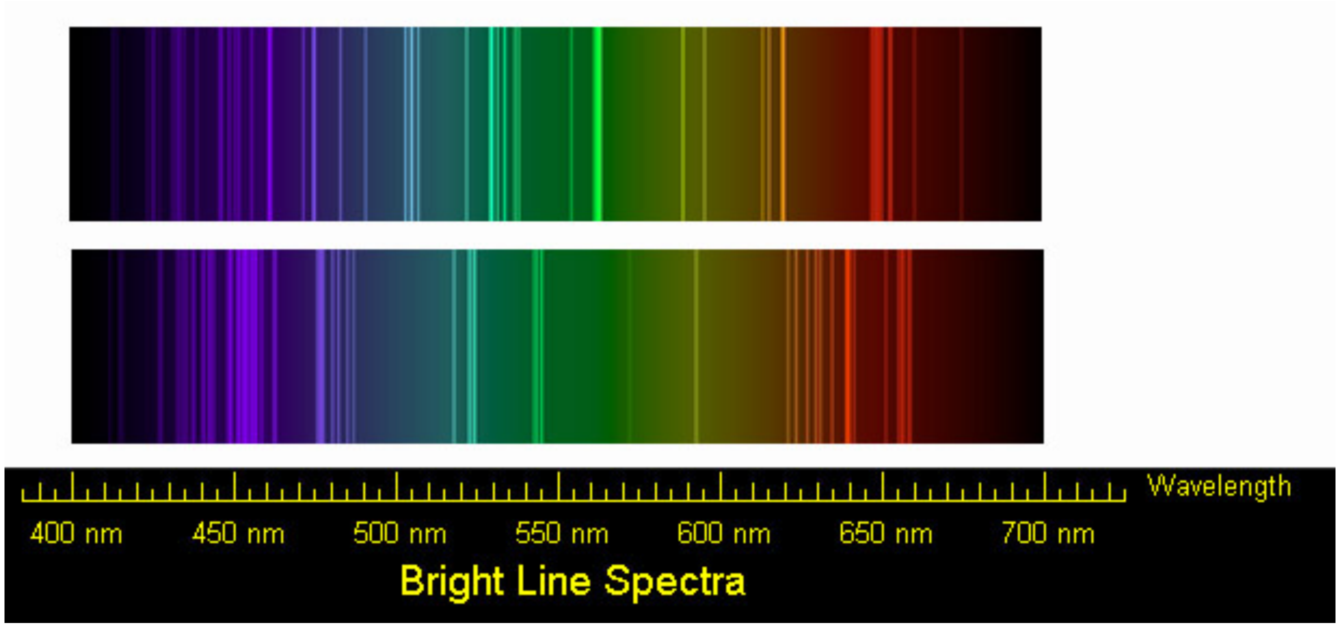
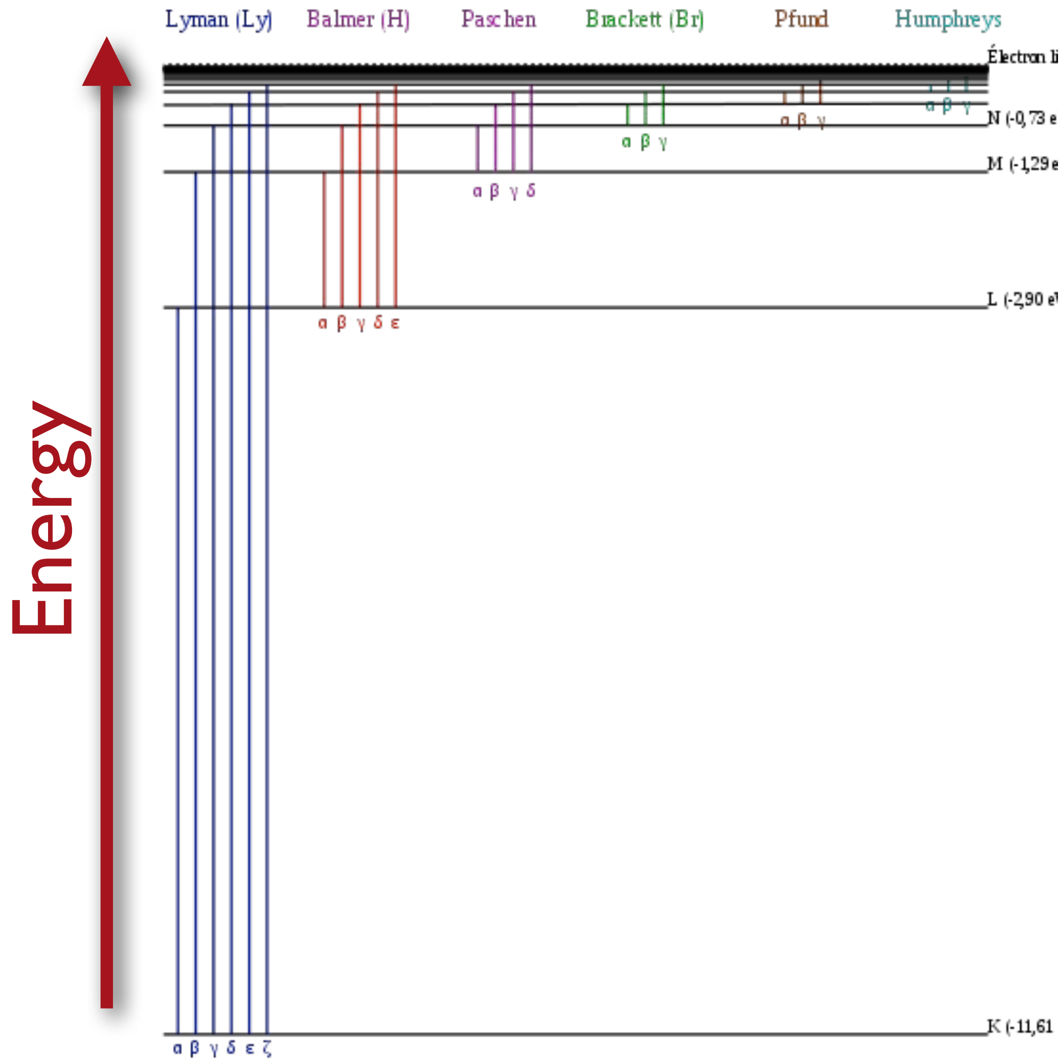


Image courtesy of NASA.

Quantization of properties



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The Double-Slit Experiment

Image of the double-slit experiment removed for copyright reasons. See the simulation at http://www.kfunigraz.ac.at/imawww/vqm/movies.html. "Samples from *Visual Quantum Mechanics*": "Double-slit Experiment."

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

Niels Bohr

Schrödinger's Cat

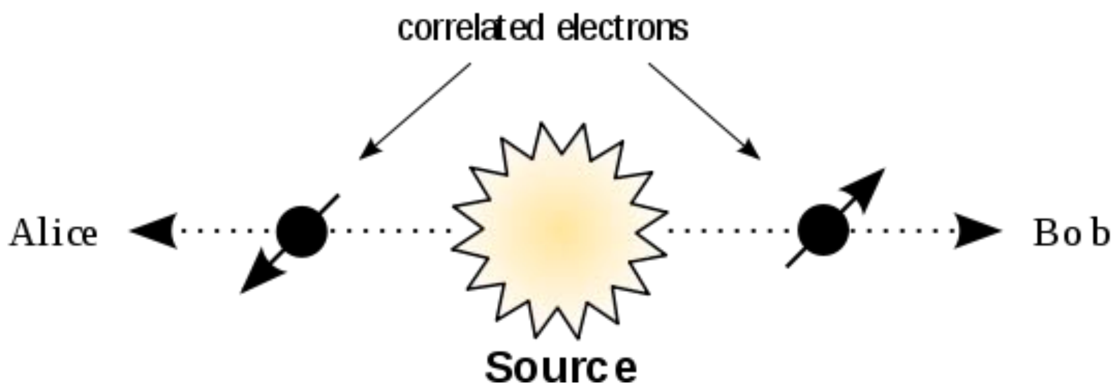
Image removed due to copyright restrictions. See the image here: http://icanhascheezburger.com/2007/06/02/im-in-ur-quantum-box/.

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

Einstein–Podolsky–Rosen



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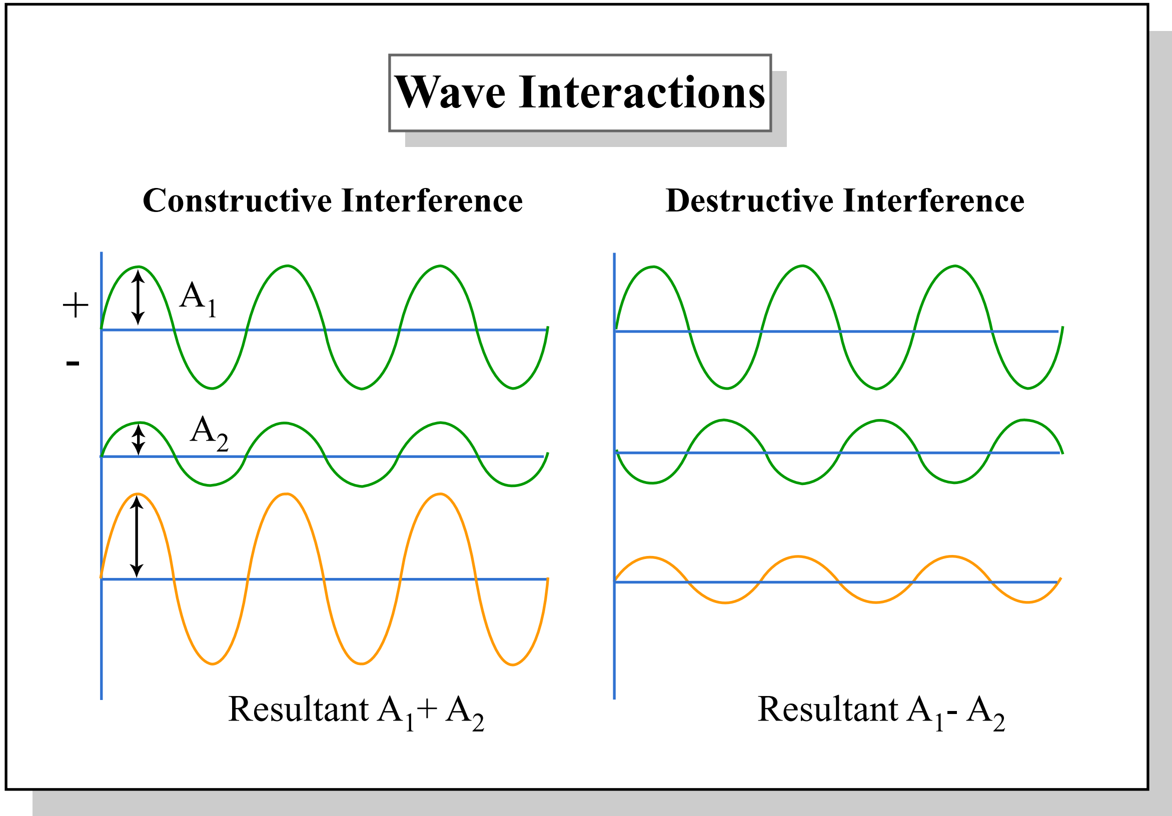
Wave-Particle Duality

- *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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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.

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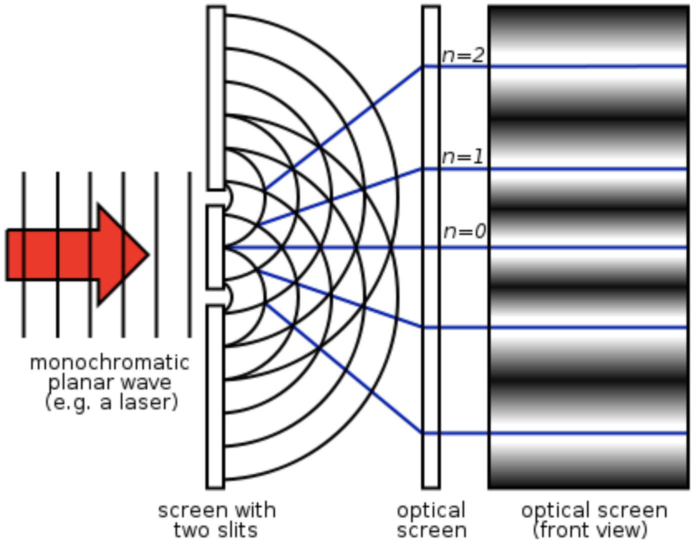
Wave aspect of matter

light
matter

wave character

particle character



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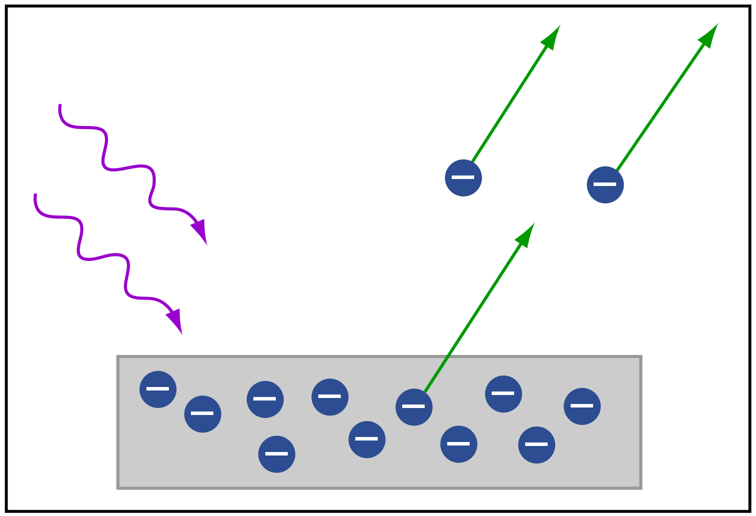

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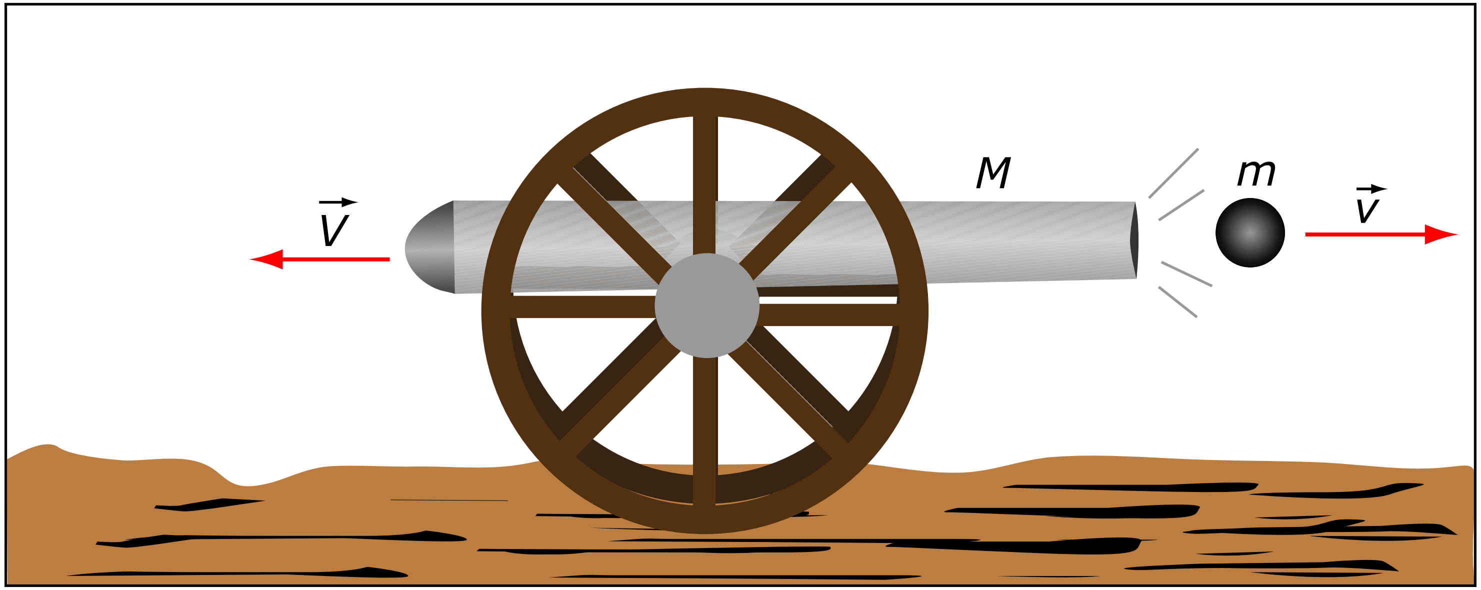
Mechanics of a Particle

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

The sum of the kinetic and potential energy is conserved.



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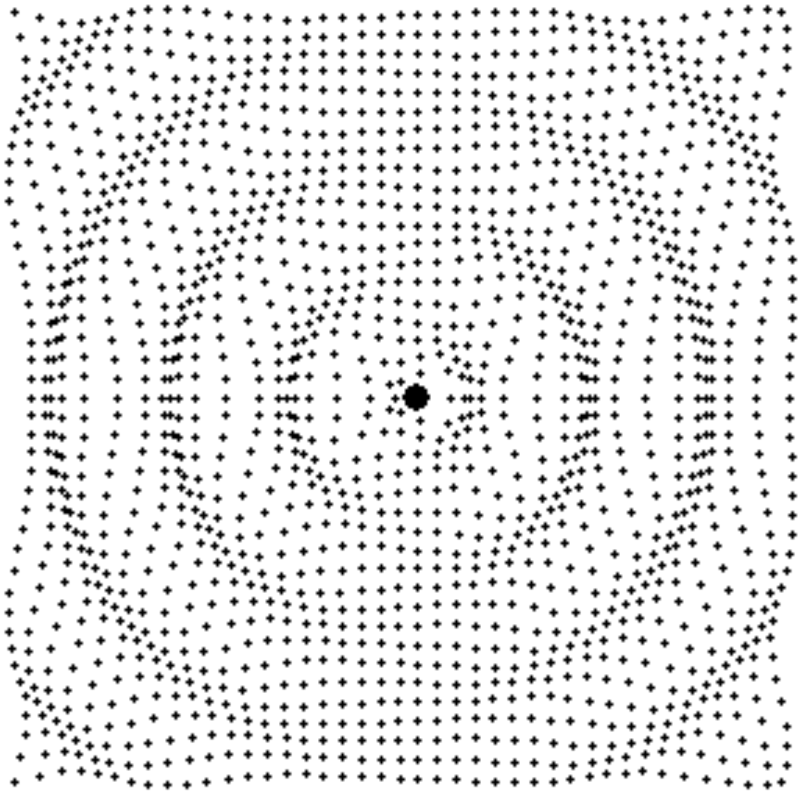
Description of a Wave



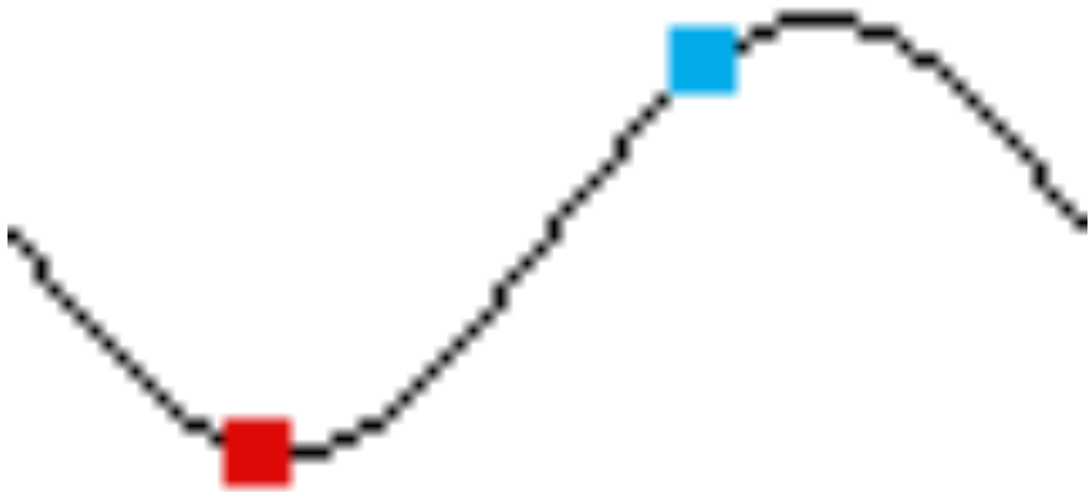
The wave is an excitation (a vibration): We need to know the amplitude of the excitation at every point and at every instant

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

Mechanics of a Wave

Free particle, with an assigned momentum:

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

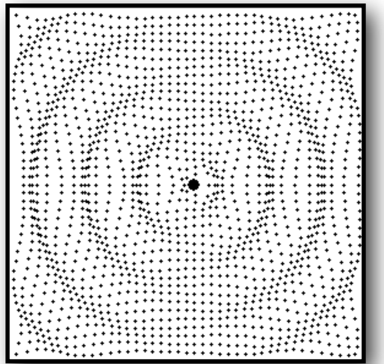


Wave aspect of matter

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

wave:

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



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

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

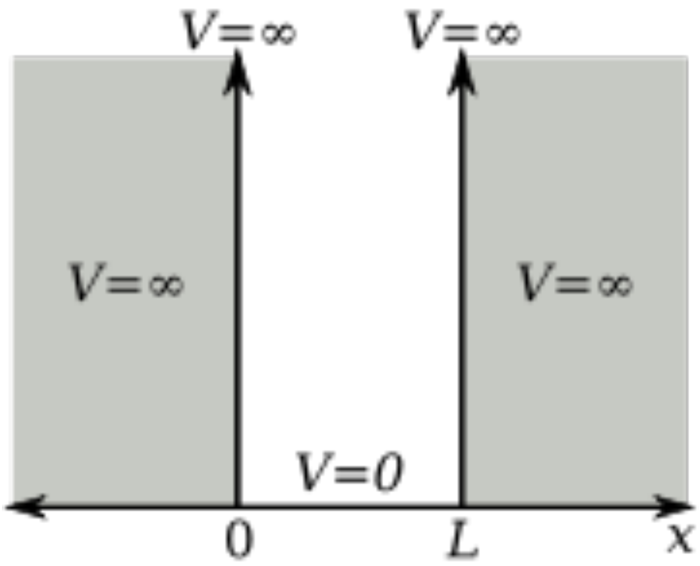
$$i\hbar \frac{\dot{f}(t)}{f(t)} = \frac{H\psi(\vec{r})}{\psi(\vec{r})} = \text{const.} = E$$

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

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

time independent Schrödinger equation
stationary Schrödinger equation

Particle in a box



Schrödinger equation

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

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

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

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

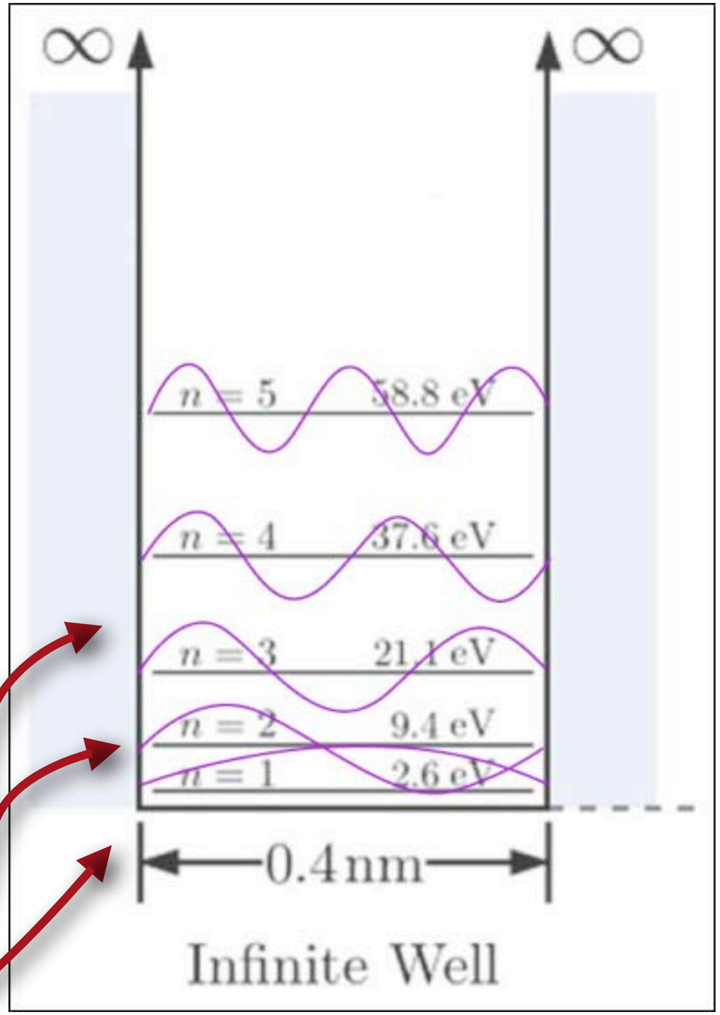
normalization

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

solution

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

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



ntum number

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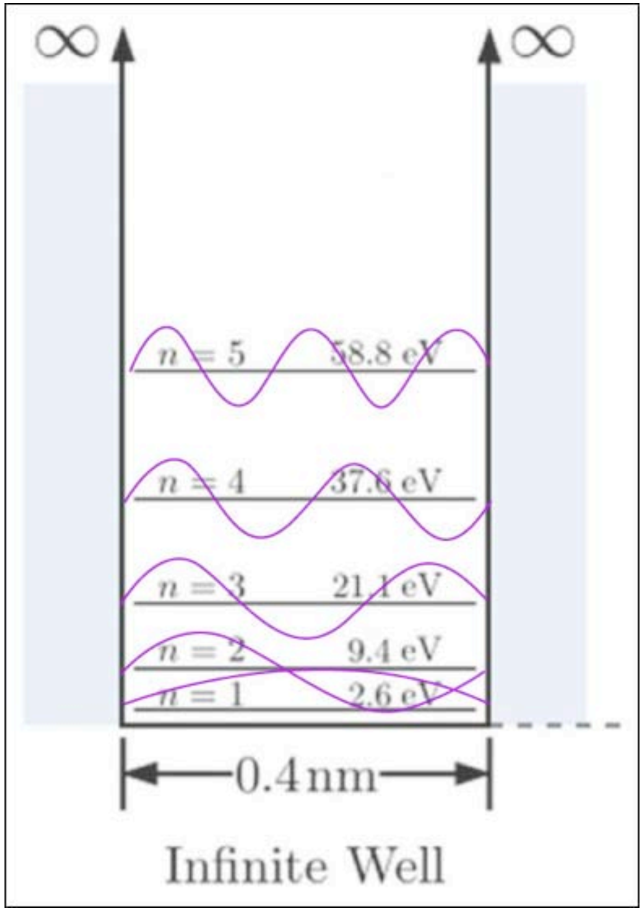
Simple examples

Electron in square well



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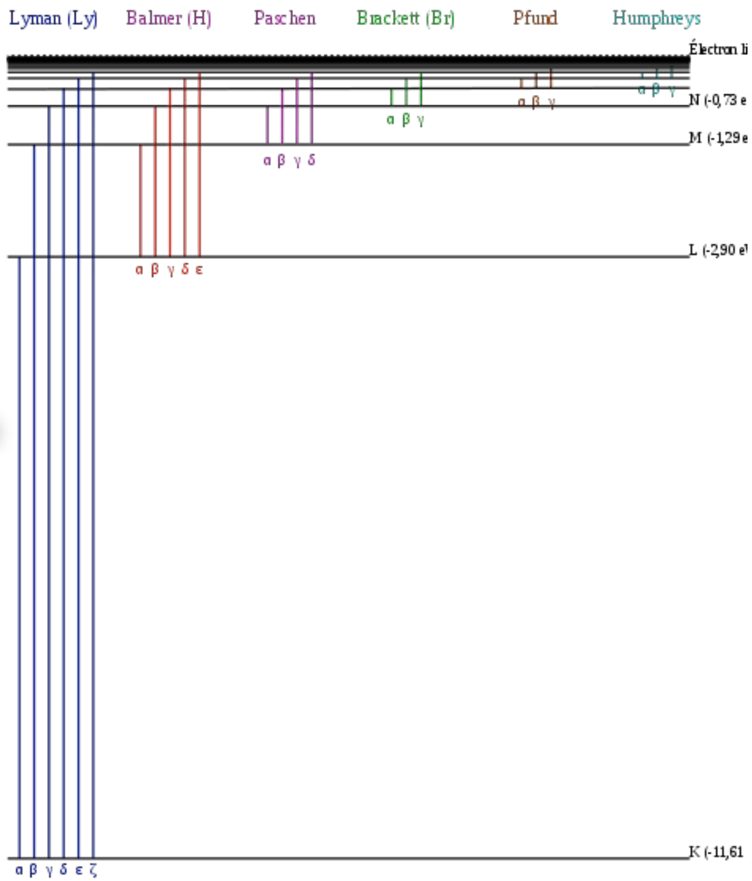

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Harmonic oscillator

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

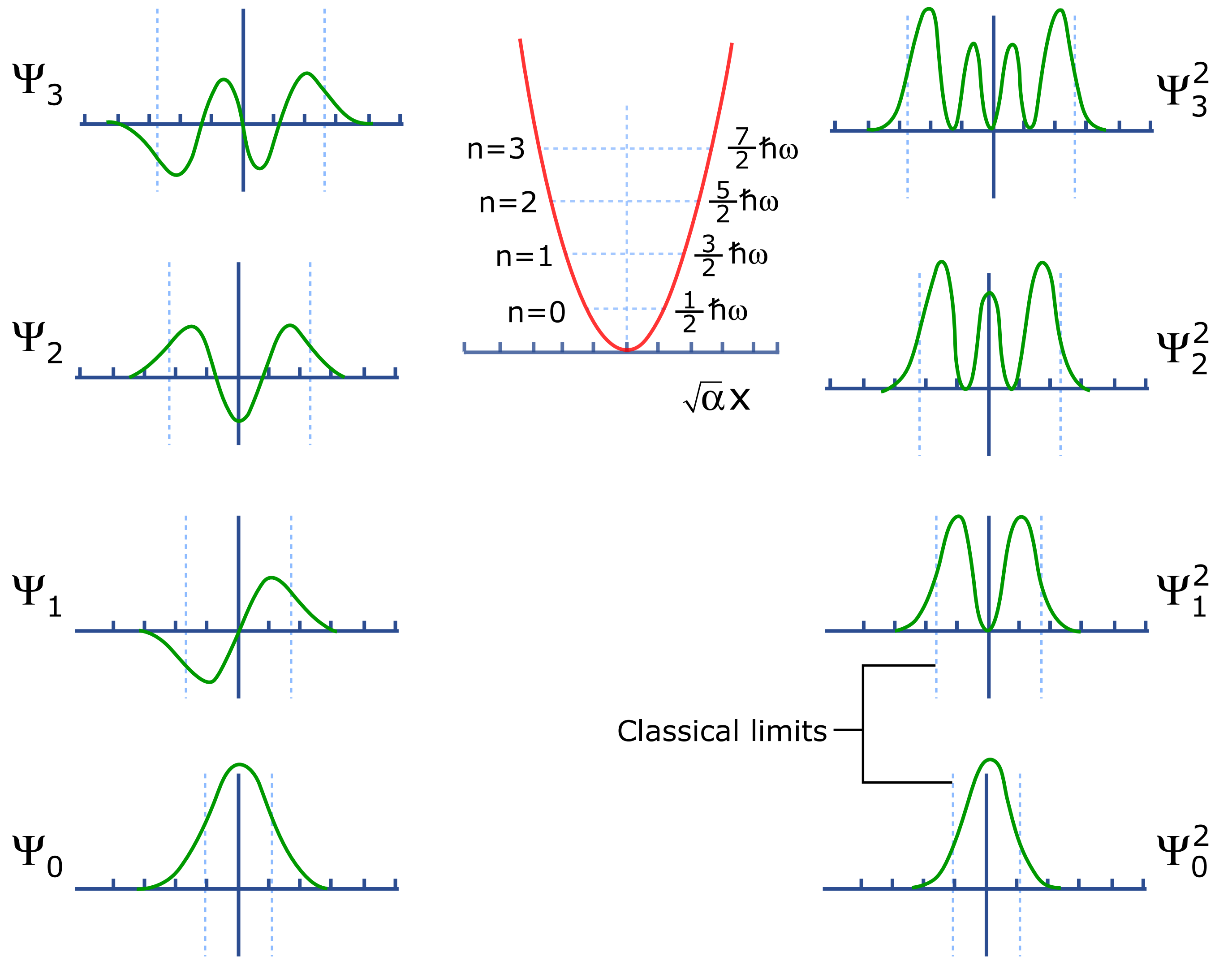
$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

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

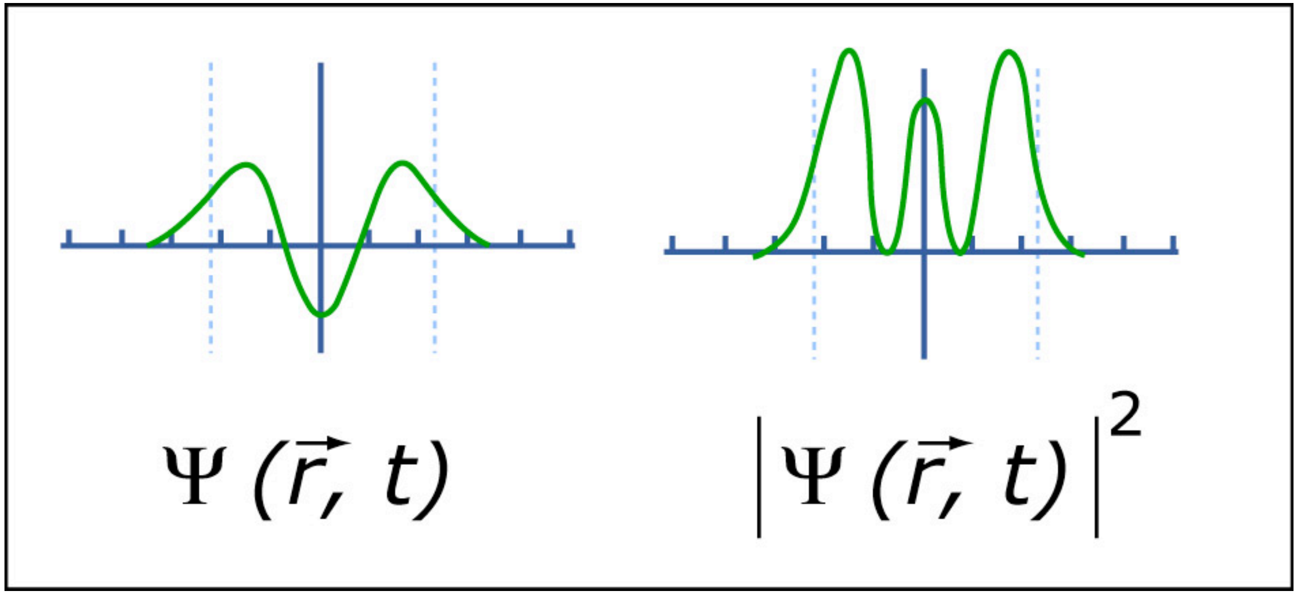


Graphs of the quantum harmonic oscillator potential and wavefunctions.

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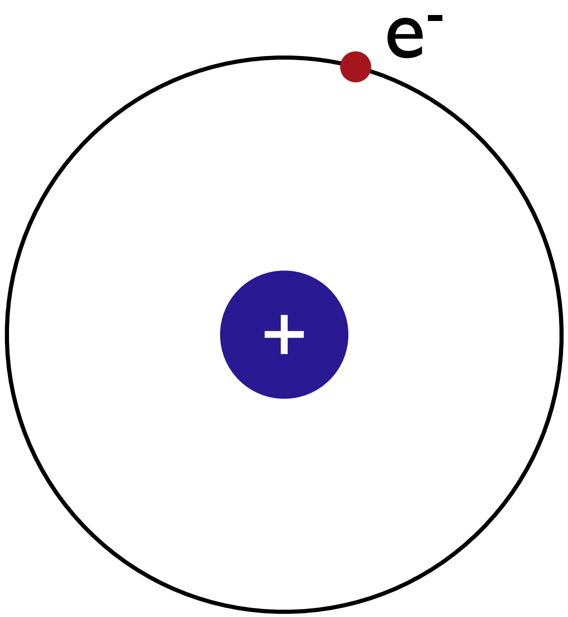
$$\int_{-\infty}^{\infty} \psi\psi^* dV = 1$$

Connection to reality?

potential: 1/r



hydrogen atom

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https://wiki.brown.edu/confluence/download/attachments/29471/HAtomOrbitals.png.

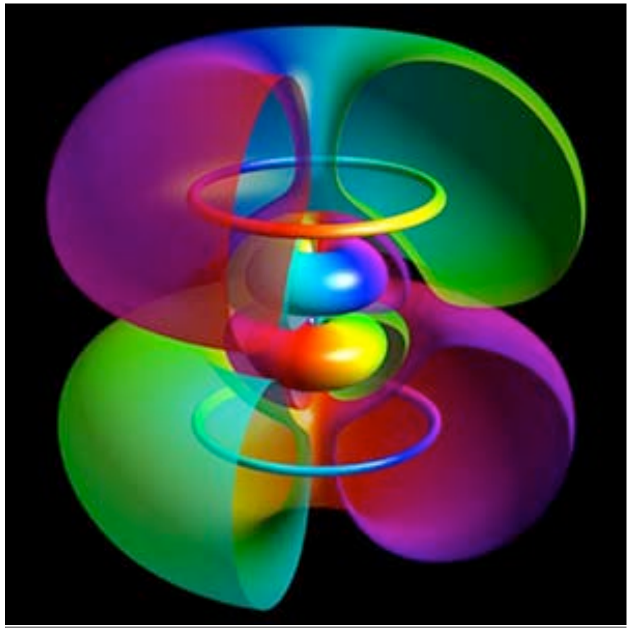
Many Interpretations of Quantum Mechanics!

http://en.wikipedia.org/wiki/Interpretations_of_quantum_mechanics#Comparison.

Source: Wikipedia

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”, ...

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