



Welcome to **CHE 384T: Computational Methods in Materials Science**

Quantum Mechanics Preliminaries



Mid-semester feedback Follow-up

Announcements

Feedback	(Proposed) changes
Pace and coverage of lectures	<ul style="list-style-type: none"> Slow pace down/more pauses Topics that will likely be cut this semester: MC, kMC, AI (cut to make room for DFT) More representative questions on pre-test (Please continue to ask questions!)
More guidance on programming assignments	<ul style="list-style-type: none"> Weekly office hours Hands-on demos in lecture & programming days Added pre-requisites, clearer course expectations
Workload for assignments	<ul style="list-style-type: none"> Assignments every 2-3 weeks (coding in ~1 week, report in ~1 week) PS5: MC cut Add guidance on choosing running parameters
Evaluation of assignments	<ul style="list-style-type: none"> Example solutions set on Canvas, HW Rubric Peer review Add example plots to lectures
Multiple ways to program	<ul style="list-style-type: none"> We do not grade for a specific implementation More guided peer review questions
Feedback on assignments	<ul style="list-style-type: none"> Please see feedback on Canvas Earlier turnaround time

Q: include DFT?



Q: handwritten notes?

Q: additional forms of guidance?



Poll will remain open until 11/01 for additional feedback

Announcements

Time to start thinking about your final project:

- Work in groups of 1-2 people
- Projects should reflect about a months worth of course time effort and should be proportional to your initial expertise (e.g., if you come from a DFT group, your final project should not be just running DFT calculations)
- Groups of 2 should propose a project that is commensurate in work with having two people on the same project. The division of work should be made clear in carrying out the project, the report, and the presentation
- Can be related to your research

Due Nov 4, 11:59pm: project proposal; [Proposal guidelines](#)

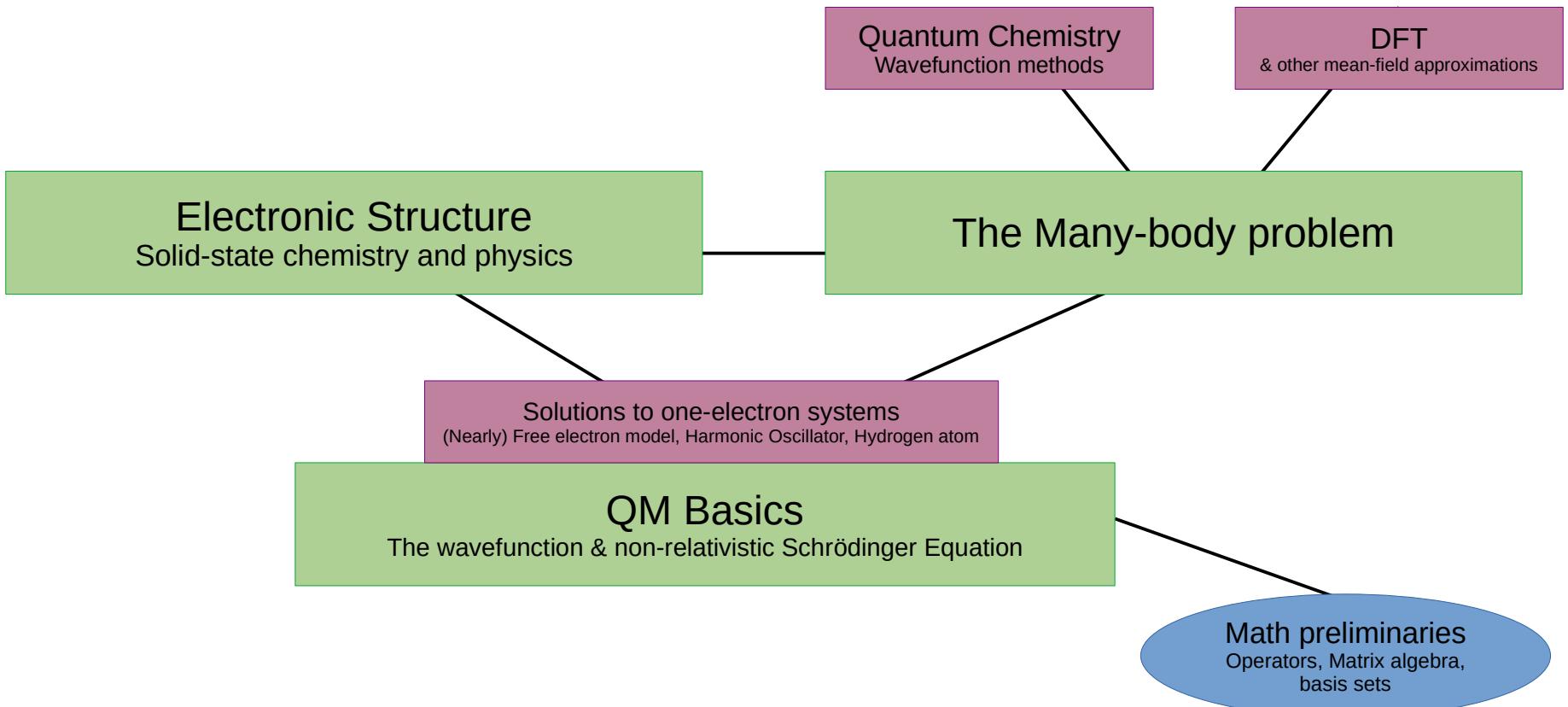
[Final Report Rubric](#)

[Final Project Presentation \(~12 min per presentation; 10 min presentation, 2 min Q&A\)](#)

Example project topics:

- Water-splitting surface reactions
- Comparison of crystalline and amorphous structure
- Grain Growth in polycrystalline structures
- Magnetic state phase diagrams with doping

Road map



Lecture Outline

Why Quantum Mechanics?

Energy scales and length in QM
Comparison with classical mechanics

De Broglie hypothesis & Wave-particle duality
Uncertainty principle

The wavefunction
Interpretations of the wavefunction
probability distributions and orthogonality

Schrodinger equation:
Time-independent and time-dependent forms

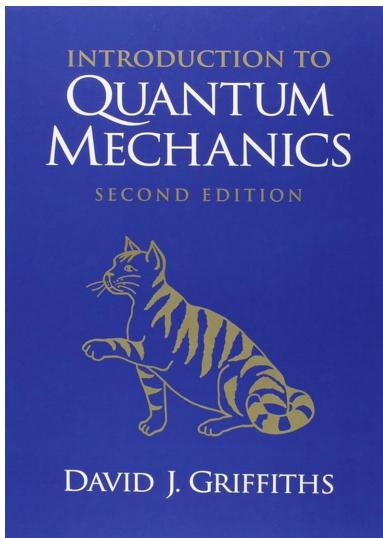
One-electron solutions of Schrodinger equation:
Free-particle and plane waves
Quantum tunneling
Free-particle in a box
Quantum harmonic oscillator
Hydrogenic atom and atomic structure

Quantum mechanics notation:

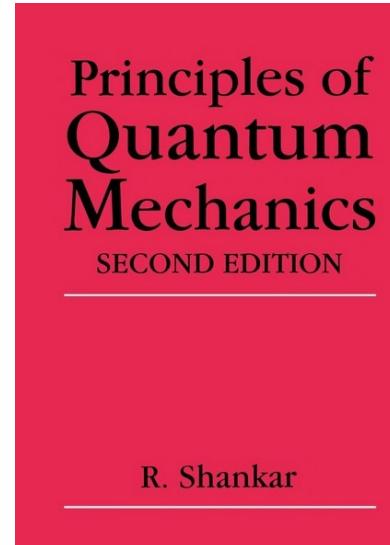
operators
expectation values and physical observables
braket notation

Preliminaries to many-body systems, DFT, and
electronic structure methods:
functionals and their derivatives
basis sets
matrix formalism of QM
variational principle

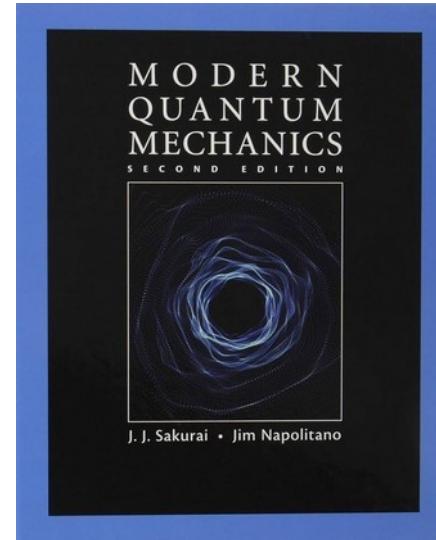
Further resources



UG level



Grad level



Grad level

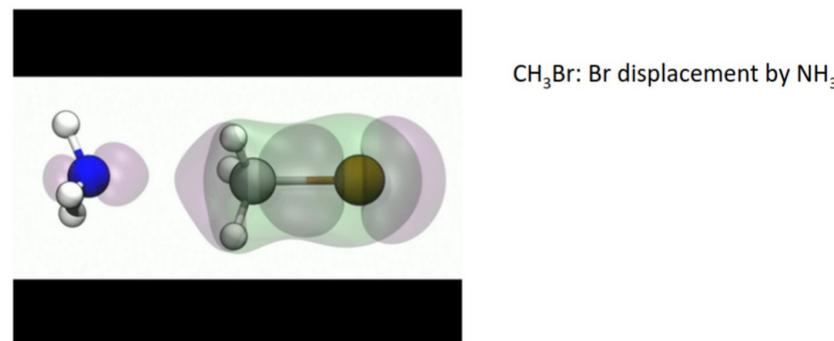
Why quantum mechanics?

Interatomic potential have limited transferability across systems and minimal theoretical basis
Dependent on interactions present (e.g., covalent, ionic, metallic)

No method to describe bond breaking

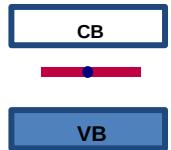
Limited information about electrons
(which give rise to electronic, optical, magnetic, chemical properties)

==> Need an *ab initio* or first-principles method for describing atoms and electrons

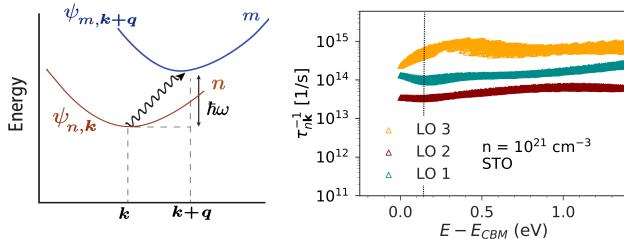


DFT gives access to electrons and nuclei

Electronic structure

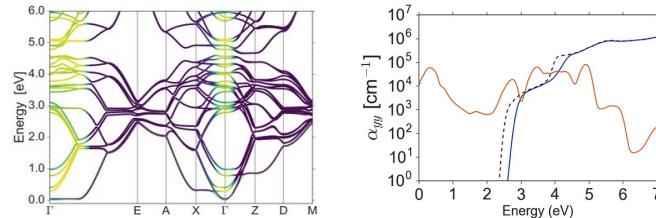


- Band structure
- Band alignments
- Carrier transport
- Optical spectra



Phonon-resolved scattering rate for understanding carrier mobilities in highly-doped systems

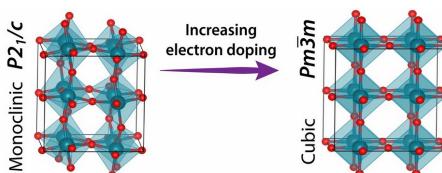
Phys. Rev. B. 101, 045116 (2020)



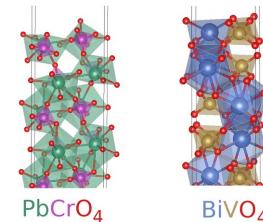
Optical matrix elements superimposed on CBs & associated absorption spectrum

MRS Communications. 8, 926-931 (2018).

Atomic structure



" J. Chem. Phys., 146, 214504 (2017)



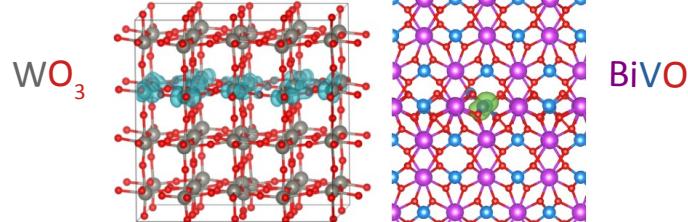
Structural changes induced by doping

Surface structure

ACS Appl. Energy Mater. 3, 8658-8666 (2020)

Charge densities

Bonding character and localization

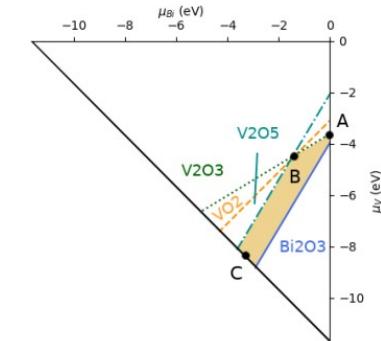
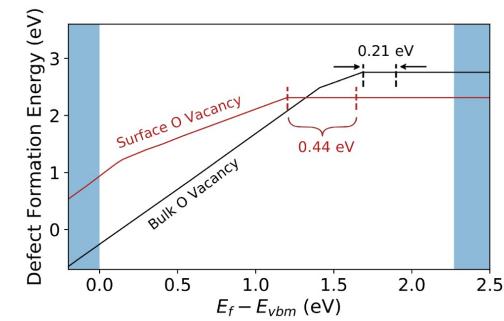


J. Mat Chem. C, 4, 6641 – 6648 (2016).

Chem. Mater. 32, 2899-2909 (2020).

Total energies

- (Defect) formation energies
- Relative stability of configurations
- Barriers to ionic motion



Chem. Mater. 32, 2899-2909 (2020).

Energy and length scales in QM

A separate set of atomic units for things at QM scale

1 unit of **charge** = absolute charge of electron = 1.60218×10^{-19} C

Energy: 1 eV = 1.60218×10^{-19} J 1 J ~ lifting an apple about 1 m

1 Hartree = 4.35981×10^{-18} J = 27.2114 eV

1 Rydberg = 0.5 Hartree = 13.6058 eV

Length: 1 Å = 10^{-10} m 10 µm ~ human hair cross-section

1 Bohr = 5.29177×10^{-11} m = 0.529177 Å

Note:

1 Bohr = radius of first orbit in Bohr's treatment of H atom

1 Hartree = energy of interaction between two electrons separated by 1 Bohr

Energy and length scales in QM

Typical length and energy scales

Thermal energy $k_B T$ at room temperature: 0.025 eV

Chemistry, differences in bonding energies within one order of magnitude of hydrogen bonding energy: 0.29 eV

Optical excitations with visible light: ~1.0 – 3.0 eV

Binding energy of electron to proton (hydrogen):
1 Rydberg = 13.6058 eV = 0.5 Hartree

Note:

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Classical v Quantum mechanics

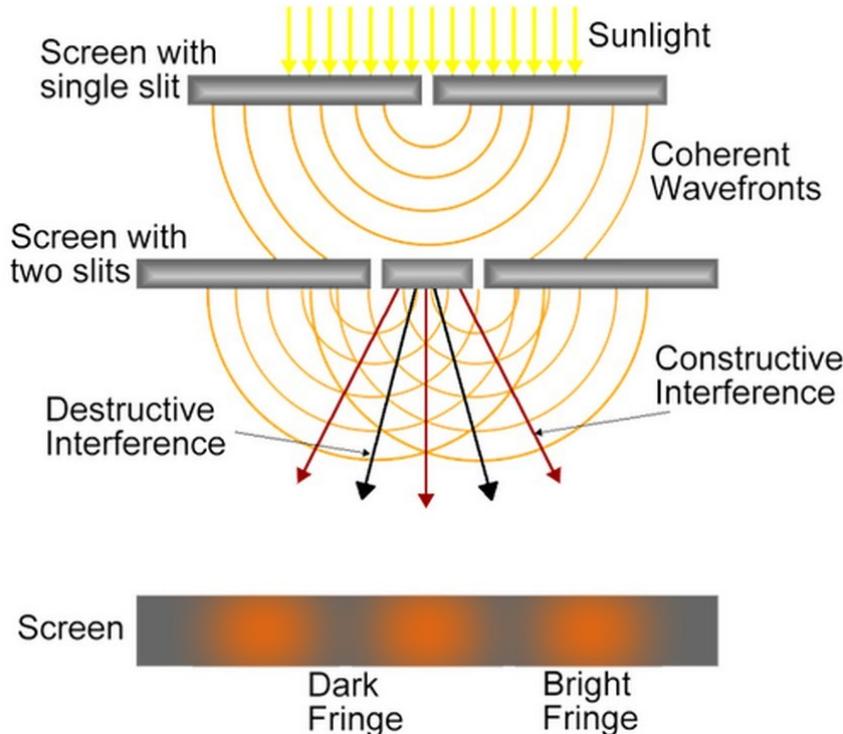
Classical Mechanics

Quantum Mechanics

What is light?

QM: De Broglie hypothesis

1801: Thomas Young, double slit experiment, diffraction through a grating → light is a wave



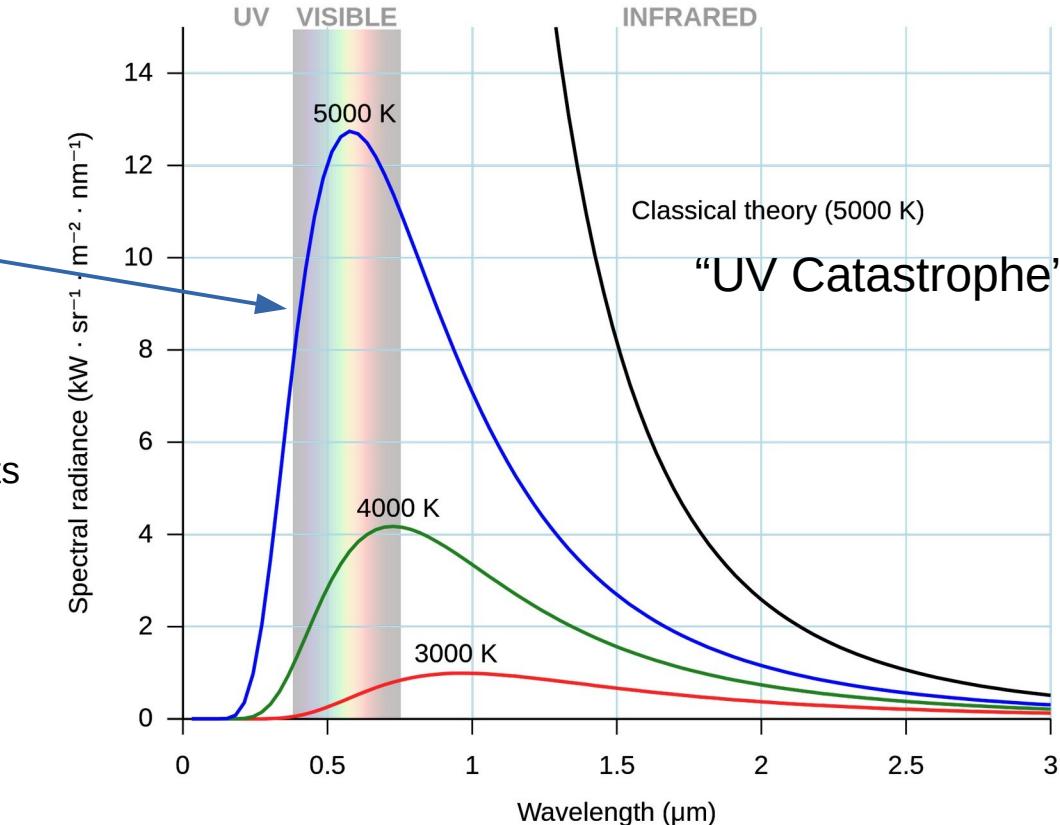
What is light?

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1801: Thomas Young, double slit experiment, diffraction through a grating → light is a wave

1900: Planck's radiation law for describing black-body radiation → light as a packet

Planck's
radiation law
correctly
anticipates
experimental
measurements



"UV Catastrophe"

But Planck
considered this
quantization as a
mathematical artifact

What is light?

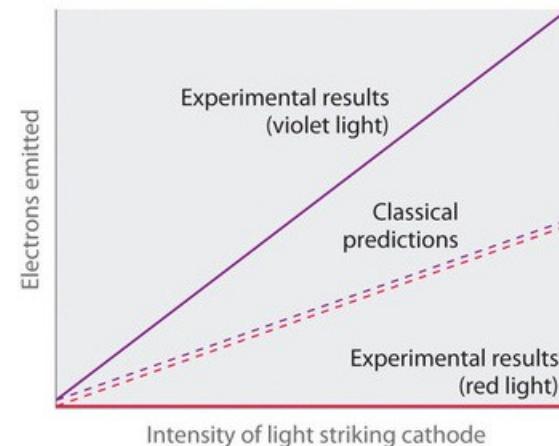
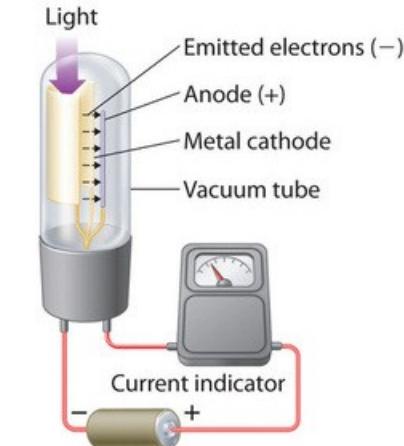
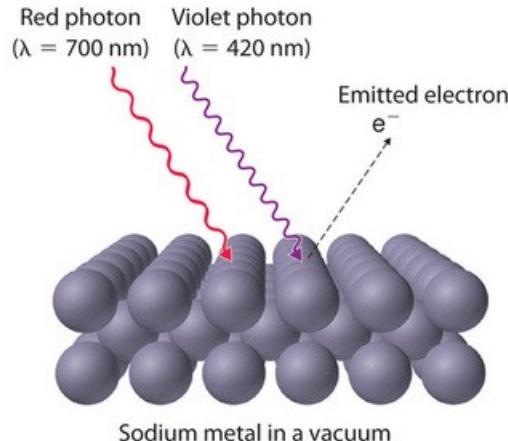
QM: De Broglie hypothesis

1801: Thomas Young, double slit experiment, diffraction through a grating → light is a wave

1900: Planck's radiation law for describing black-body radiation → light as a packet

1905: Einstein, photoelectric effect → light is a particle, **quantized** in packets called photons
Recognized that this quantization is physically meaningful

Each metal has a characteristic threshold frequency of light $E_o = hf$ for ejection of electrons



ChemLibre Texts

Classical mechanics prediction: electrons should be emitted regardless of light

Actual: electrons only emitted for $E > E_o$ where $KE_e = E - E_o$

Intensity of light ~ number of photons
Frequency of light ~ energy of photon

What is matter?

QM: De Broglie hypothesis

1924: De Broglie, PhD thesis, all matter is a wave, with characteristic wavelength

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

$$h = 4.125667 \times 10^{-15} \text{ eV} \cdot \text{s} = 6.626070 \times 10^{-34} \text{ J} \cdot \text{s}$$

$$\hbar = h/(2\pi) = 6.582119 \times 10^{-16} \text{ eV} \cdot \text{s} = 1.054571 \times 10^{-34} \text{ J} \cdot \text{s}$$

Heuristic basis (but not really a derivation):

Assume

$$E = h\nu_0 = mc^2$$

In frame of moving particle:
Some time dilation, relativistic effects

$$\nu_1 = \nu_0 \sqrt{1 - \frac{v^2}{c^2}}$$

SÉANCE DU 10 SEPTEMBRE 1923.

507

RADIATIONS. — *Ondes et quanta* (¹). Note de M. LOUIS DE BROGLIE,
présentée par M. Jean Perrin.

Considérons un mobile matériel de masse propre m_0 se mouvant par rapport à un observateur fixe avec une vitesse $v = \beta c$ ($\beta < 1$). D'après le principe de l'inertie de l'énergie, il doit posséder une énergie interne égale à $m_0 c^2$. D'autre part, le principe des quanta conduit à attribuer cette énergie interne à un phénomène périodique simple de fréquence ν_0 telle que

$$h\nu_0 = m_0 c^2,$$

c étant toujours la vitesse limite de la théorie de relativité et \hbar la constante de Planck.

Pour l'observateur fixe, à l'énergie totale du mobile correspondra une fréquence $\nu = \frac{m_0 c^2}{\hbar \sqrt{1 - \beta^2}}$. Mais, si cet observateur fixe observe le phénomène périodique interne du mobile, il le verra ralenti et lui attribuera une fré-

To a stationary observer

$$h\nu = \frac{hc}{\lambda} = \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$$\lambda = \frac{h}{mc} \sqrt{1 - \frac{v^2}{c^2}}$$

For a non-relativistic object

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

(¹) Au sujet de la présente Note, voir M. BRILLOUIN, *Comptes rendus*, t. 168, 1919, p. 1318.

What is matter?

QM: De Broglie hypothesis

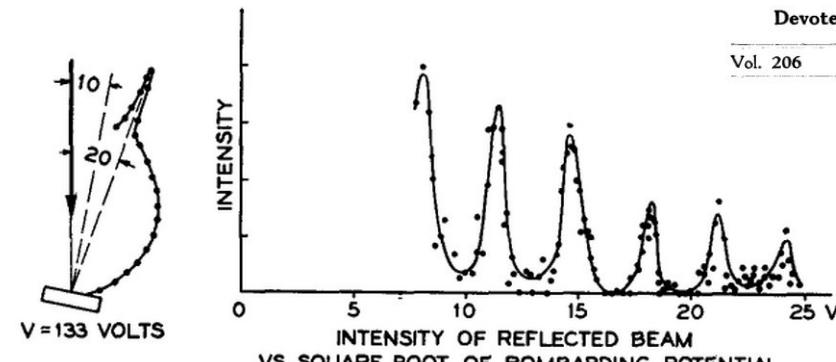
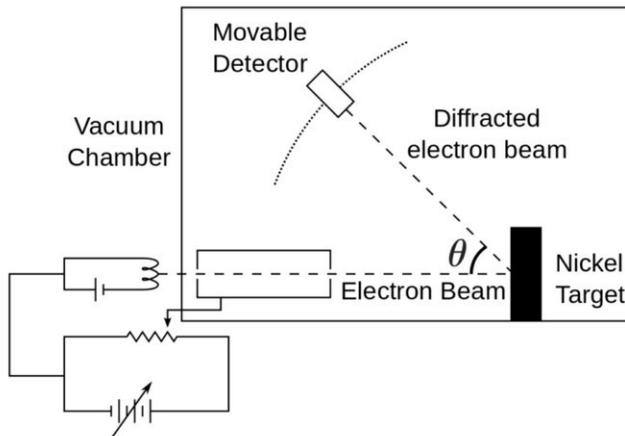
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1927: experimental validation from Davisson and Germer
electron scattering shows diffraction patterns!



Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 206

MAY, 1928

No. 5

ARE ELECTRONS WAVES? *

BY
C. J. DAVISSON, Ph.D.
Bell Telephone Laboratories, Inc.

This is often considered the starting point for matter wave mechanics, i.e., quantum mechanics

What is matter?

QM: De Broglie hypothesis

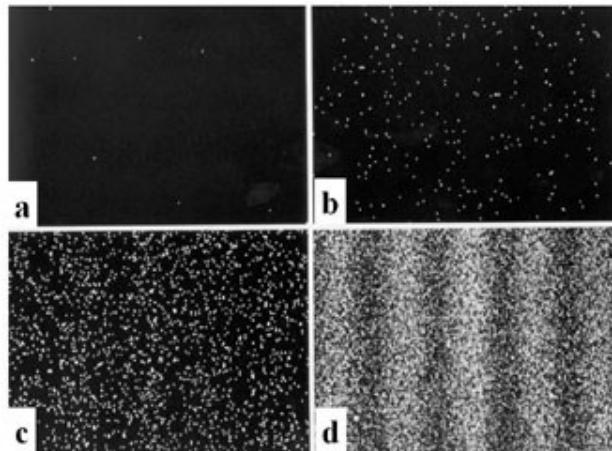
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1989: Tonomura and colleagues at Hitachi, single-electron buildup of interference



Single-electron events built up over 20 minute exposure for double-slit experiment. (a) 8 electrons, (b) 270 electrons, (c) 2000 electrons, (d) 60,000 electrons

Demonstration of single-electron buildup of an interference pattern

A. Tonomura, J. Endo, T. Matsuda, and T. Kawasaki
Advanced Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185, Japan

H. Ezawa
Department of Physics, Gakushuin University, Mejiro, Tokyo 171, Japan

(Received 17 December 1987; accepted for publication 22 March 1988)

The wave-particle duality of electrons was demonstrated in a kind of two-slit interference experiment using an electron microscope equipped with an electron biprism and a position-sensitive electron-counting system. Such an experiment has been regarded as a pure thought experiment that can never be realized. This article reports an experiment that successfully recorded the actual buildup process of the interference pattern with a series of incoming single electrons in the form of a movie.

A historical account into the debated attribution of findings related to the double-slit experiment:

<https://physicsworld.com/a/the-double-slit-experiment/>

Was a by-product of research into more practical applications of electron interferometry

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Wave-particle duality: characteristics of both wave and particles

Typical De Broglie wavelengths and length scales:

- Atom diameter $\sim 1 \text{ \AA} = 0.1 \text{ nm}$
- Electron accelerated through 100 V: $\lambda \sim 0.12 \text{ nm}$
- Baseball traveling at 90 mph: $\lambda \sim 10^{-25} \text{ nm}$

De Broglie wavelength of macroscopic objects is negligible
i.e., particle-like character is dominant

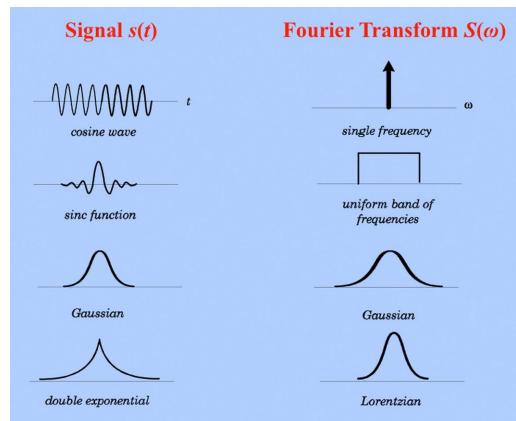
QM: Uncertainty principle

The position x and momentum p cannot be simultaneously measured with arbitrarily high precision.

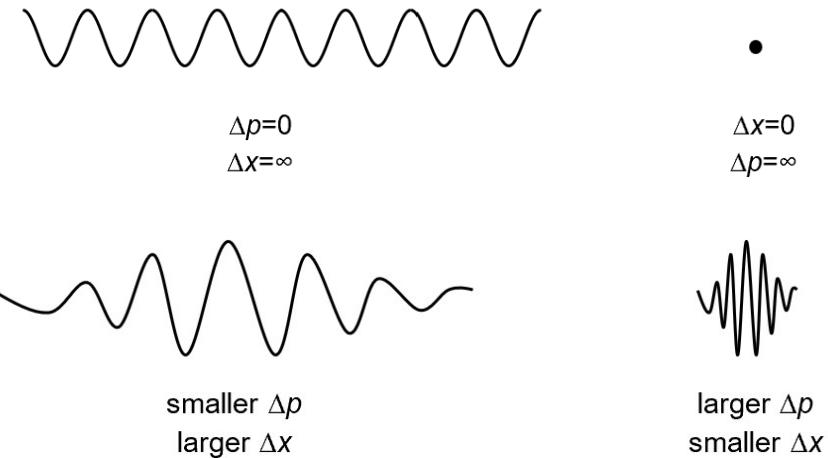
$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

A similar relation b/t energy & time

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$



As a consequence of wave-particle duality



A particle is like a localized wave

QM: The Wavefunction

The wavefunction fully describes the state of the system

A differentiable, complex function

$$\psi(r, t)$$

Itself is not a physical observable

The statistical interpretation

$$|\Psi(x, t)|^2 dx = \left\{ \begin{array}{l} \text{probability of finding the particle} \\ \text{between } x \text{ and } (x + dx), \text{ at time } t. \end{array} \right\}$$

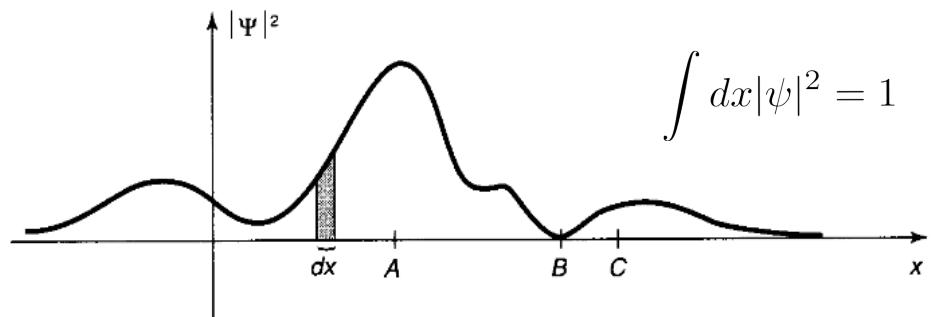


Figure 1.2: A typical wave function. The particle would be relatively likely to be found near *A*, and unlikely to be found near *B*. The shaded area represents the probability of finding the particle in the range dx .

Griffiths, Introduction to Quantum Mechanics

$$\rho(r, t) = |\psi(x, t)|^2 = \psi^*(x, t)\psi(x, t)$$

QM: the Wavefunction

The Copenhagen interpretation:

Before measurement, the particle can be in a superposition of multiple states

After measurement, the act of measurement collapses the wavefunction
(which spreads out again in accordance to the Schrodinger equation)

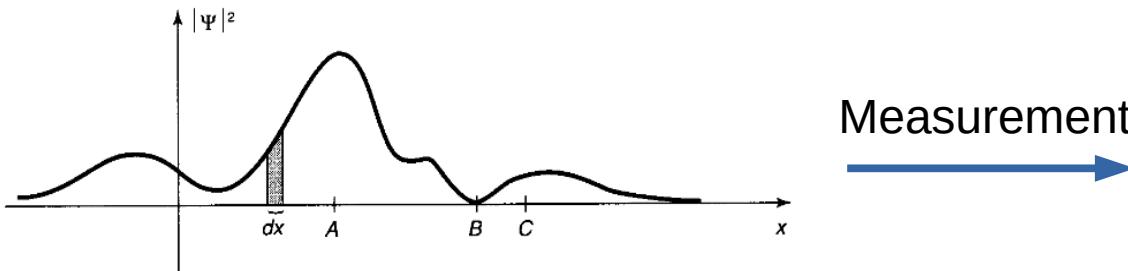


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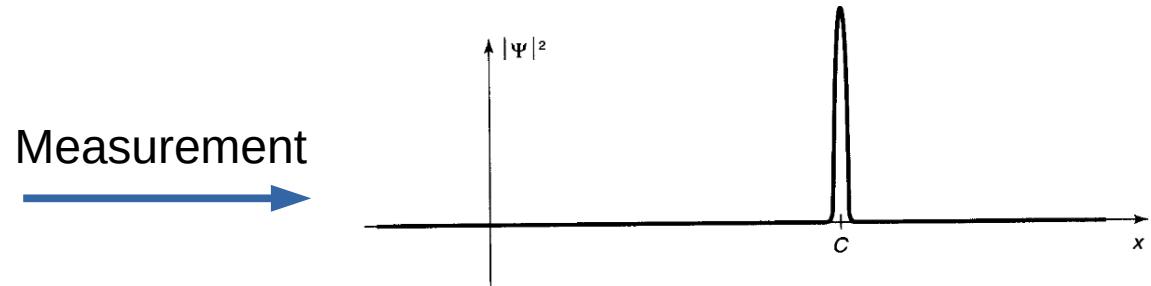
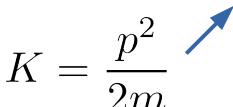


Figure 1.3: Collapse of the wave function: graph of $|\Psi|^2$ immediately after a measurement has found the particle at point C .

QM: Schrodinger equation

Time-*dependent* form

Wave equation of motion is a linear partial differential equation

$$\Psi(x, t) \quad i\hbar \frac{\partial \Psi}{\partial t} = \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi$$
$$K = \frac{p^2}{2m}$$


Time-*independent* form

Consider a time-independent potential

$$U(x, t) \rightarrow U(x)$$

$$\Psi(x, t) = \psi(x)f(t)$$

Insert into time-dependent form to get two linear differential equations

QM: Schrodinger equation

Time-*independent* form

Solve for the time function $i\hbar \frac{df(t)}{dt} = Ef(t)$

$$f(t) = Ae^{-iEt/\hbar}$$

Solve for the position function will depend on the potential and involves more work

$$\hat{H}\psi = E\psi$$

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \psi(x) = \underline{E}\psi(x)$$

Eigenvalue

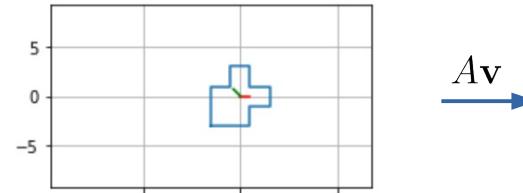
$$\Psi(x, t) = \underline{\psi(x)} e^{-iEt/\hbar}$$

Eigenvector
Eigenstate

Linear algebra: eigenvalues and eigenvectors

Eigenvector = characteristic vector \mathbf{v} that is scaled by its eigenvalue upon linear transformation matrix A

'eigen' = German for 'own'



In QM, eigenvectors or eigenstates are called "stationary states", because the position probability density does not depend on time

$$\hat{H}\psi = E\psi$$

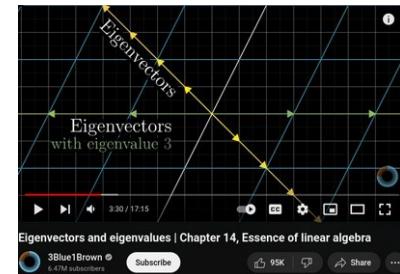
$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

$$\rho(r, t) = |\Psi(r, t)|^2 = \Psi^* \Psi = \rho(r)$$

Only need to solve for the time-independent (position) $\psi(x)$

Can construct the time-dependent solution from eigenvalues (allowed energy levels) and eigenfunctions (wavefunctions)

A nice graphical refresher from 3Blue1Brown



One-particle solutions to Schrodinger equation

Case 1: Free particle (1D)

Schrodinger equation:

Solutions

One-particle solutions to Schrodinger equation

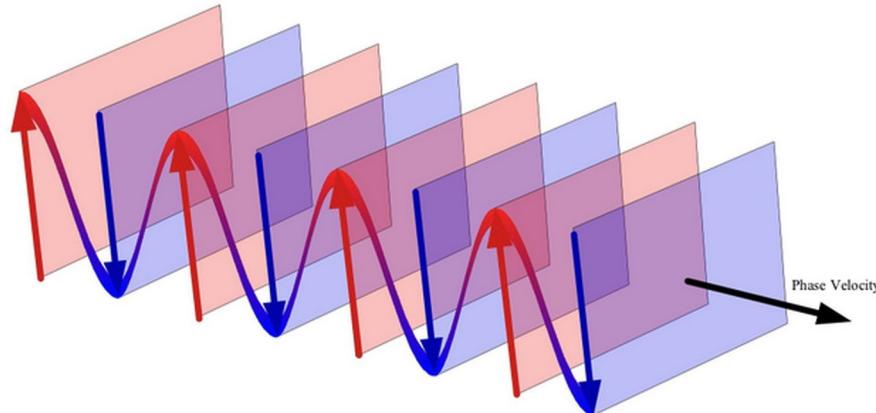
Case 1: Free particle (1D)

The plane wave

$$\Psi(x, t) = \psi(x)e^{-i(kx - Et/\hbar)}$$
$$= \psi(x)e^{-i(kx - \omega t)}$$

$$k = \frac{\sqrt{2mE}}{\hbar}$$

$$E = \hbar\omega$$



Delocalized in position space
Fully localized in momentum space

$$\mathbf{p} = \hbar\mathbf{k}$$

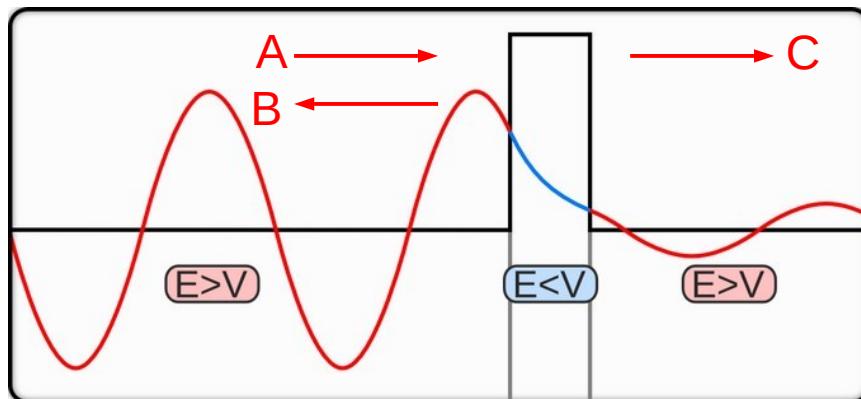
One-particle solutions to Schrodinger equation

Case 1: Free particle (1D)

Example: Scattering and tunneling

$$k = \frac{\sqrt{2mE}}{\hbar}$$

$$\kappa = \frac{\sqrt{2m(V - E)}}{\hbar}$$



$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

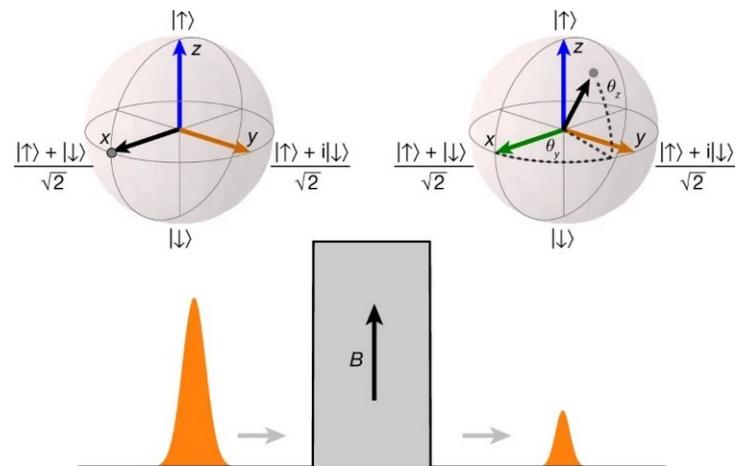
$$\psi(x) = Fe^{ikx}$$

$$\psi(x) = Ce^{-\kappa x} + De^{\kappa x}$$

Transmission/tunneling probability:

$$T = \left| \frac{F}{A} \right|^2$$

Measuring the time the particle spends in the barrier: Larmor clock



Nature 583, 529–532 (2020).

Use polarized spin-1/2 particles
Apply a magnetic field B in the barrier

Measure spin precession $\theta = \omega_L \tau$

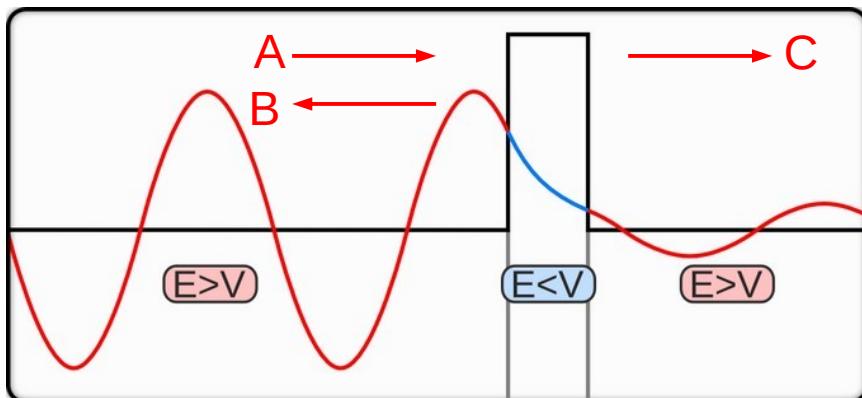
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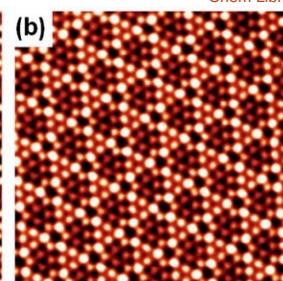
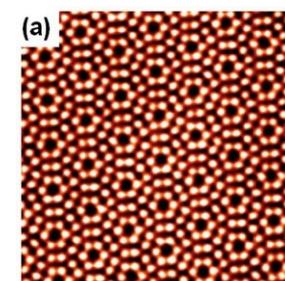
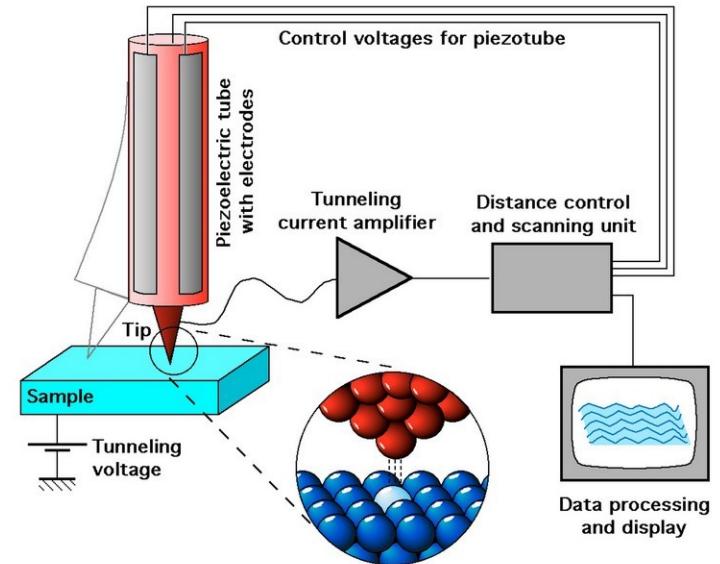
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$$T = \left| \frac{F}{A} \right|^2$$

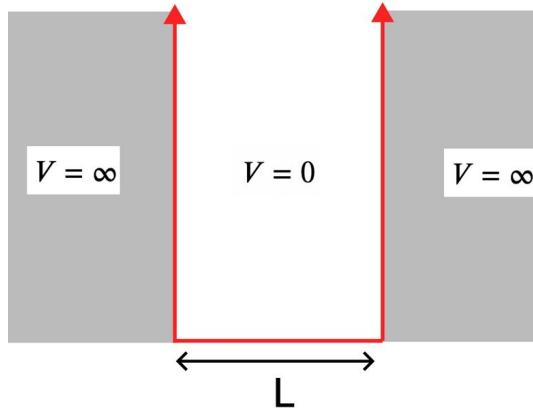
Measuring surfaces with STM



STM of surface reconstruction in silicon

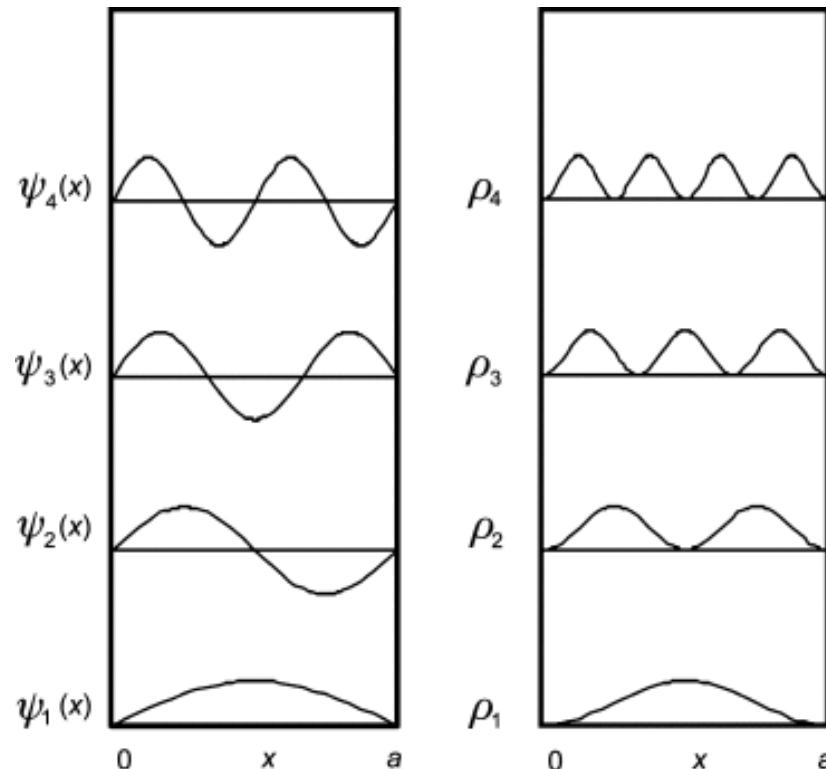
One-particle solutions to Schrodinger equation

Case 2: Free particle in a box



One-particle solutions to Schrodinger equation

Case 2: Free particle in a box



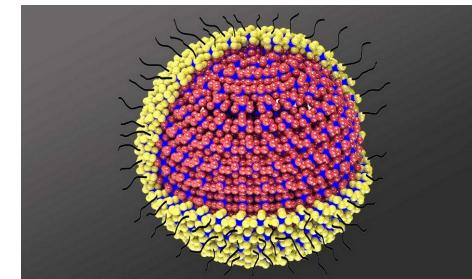
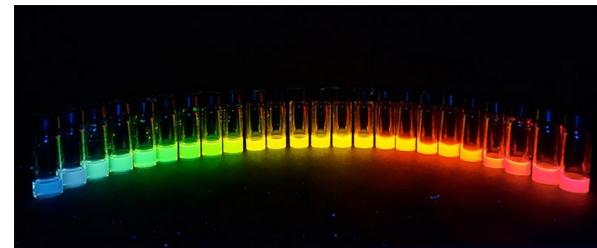
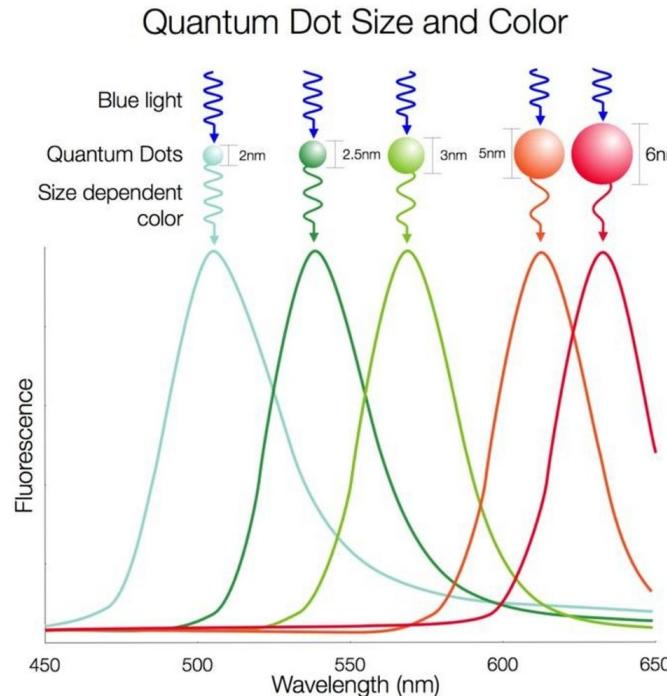
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2m L^2} n^2$$

One-particle solutions to Schrodinger equation

Case 2: Free particle in a box

Example: Quantum dots, particle in a box confined in 3D



One-particle solutions to Schrodinger equation

Case 3: Quantum harmonic oscillator

Useful because a local minimum in the potential energy can always be expanded as a parabola

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \right] \psi_n(x) = E_n \psi_n(x)$$

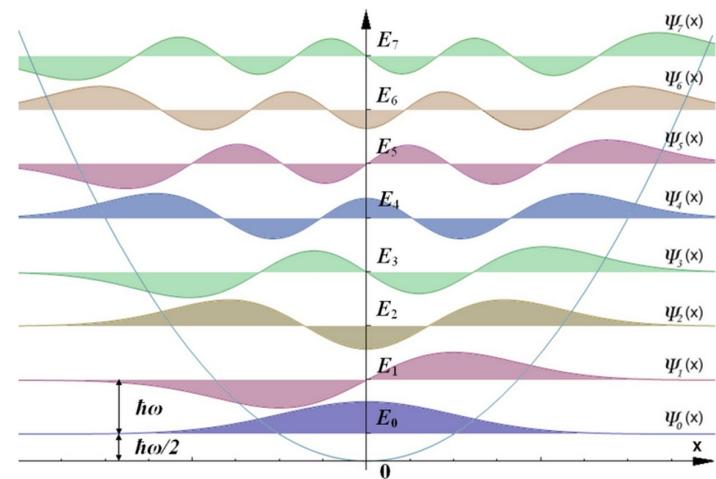
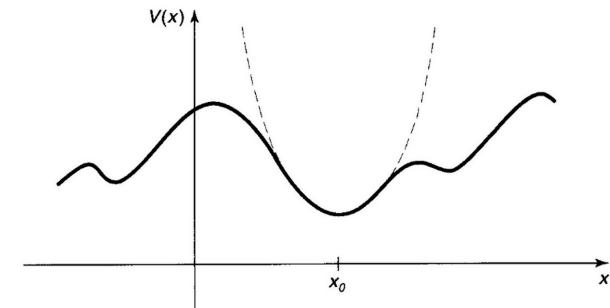
$$\omega \equiv \sqrt{\frac{k}{m}} \quad \frac{1}{2} kx^2 \rightarrow \frac{1}{2} m\omega^2 x^2$$

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

Wavefunctions consists of Hermite Polynomials, generated from ground state

$$\psi_0(x) = A_0 \exp\left(-\frac{m\omega}{2\hbar}x^2\right) \quad \text{Ground state}$$

$$\psi_n(x) = A_n (\hat{a}_+)^n \exp\left(-\frac{m\omega}{2\hbar}x^2\right) \quad \text{Excited states}$$



One-particle solutions to Schrodinger equation

Case 3: Quantum harmonic oscillator

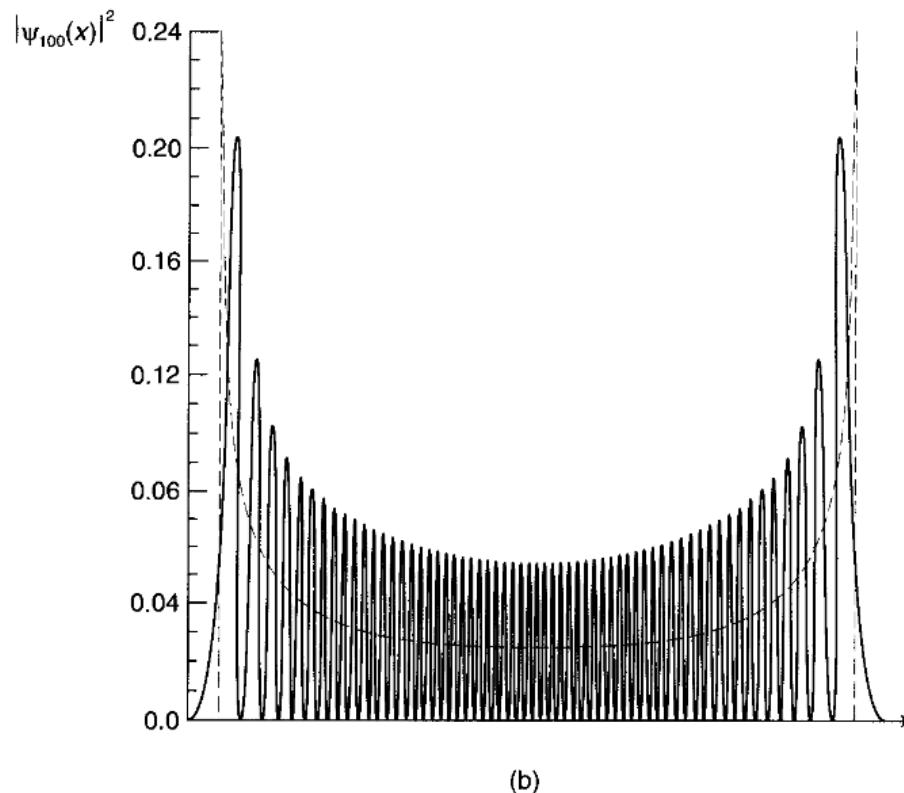
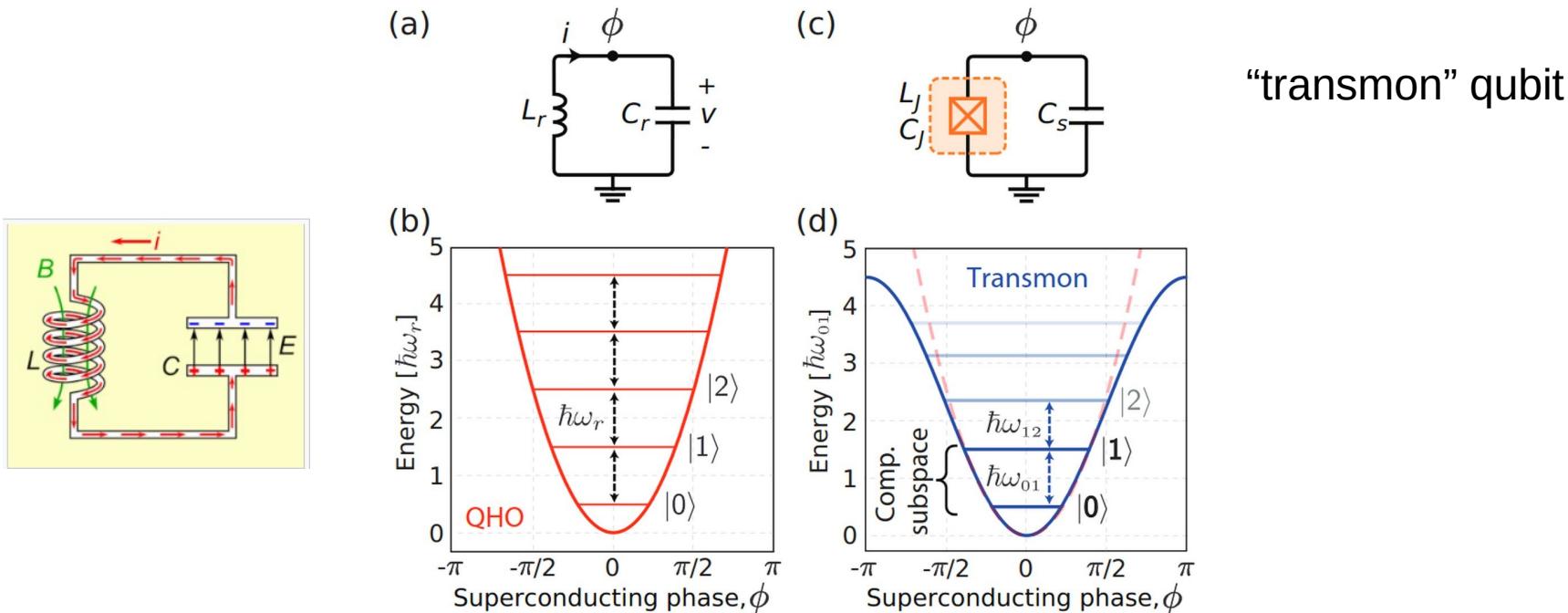


Figure 2.5: (a) The first four stationary states of the harmonic oscillator.
(b) Graph of $|\psi_{100}|^2$, with the classical distribution (dashed curve) superimposed.

One-particle solutions to Schrodinger equation

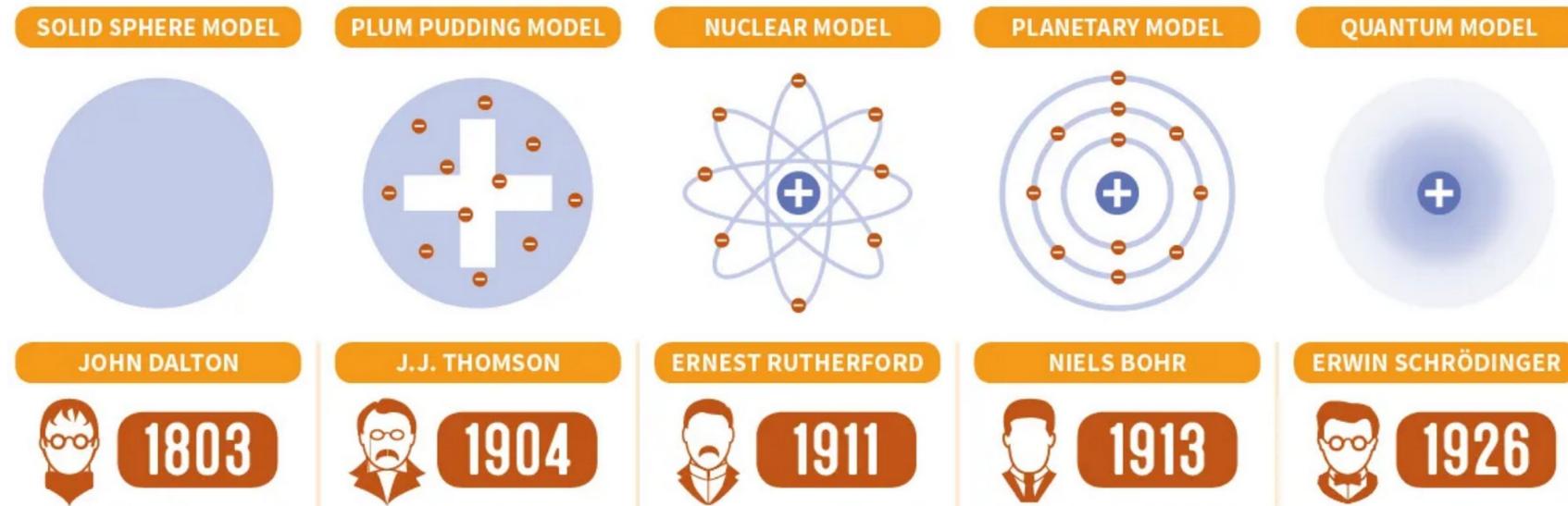
Case 3: Quantum harmonic oscillator

Example: superconducting qubits

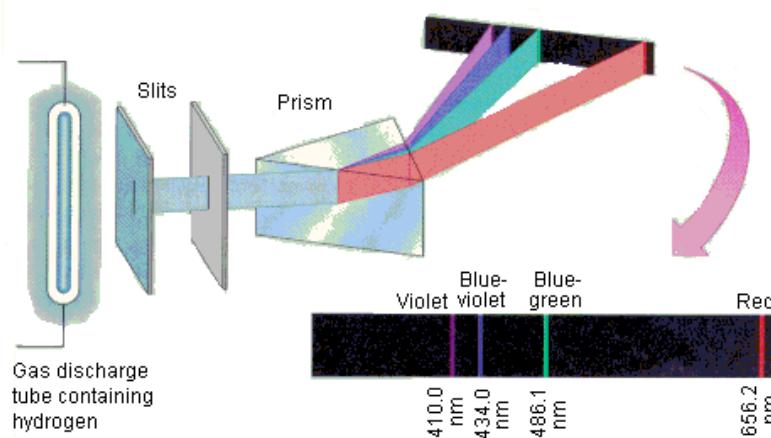


One-particle solutions to Schrodinger equation

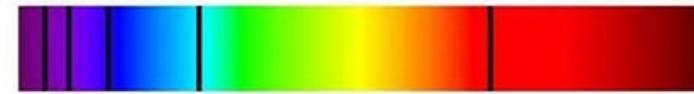
Case 4: Hydrogen atom



Structure of the atom



Hydrogen Absorption Spectrum



Hydrogen Emission Spectrum



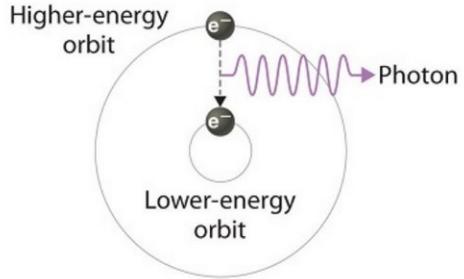
1862: Anders Ångström uses diffraction gratings to study the emission spectra of Hydrogen

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

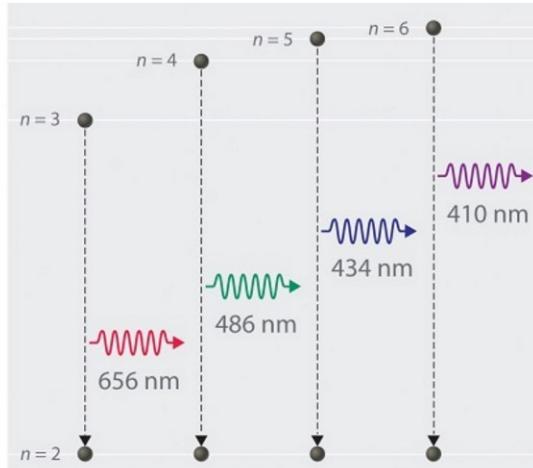
1880s – 1908: refinement of Hydrogen spectra and search to
rationalize from where these spectral lines come
using experimental data

Structure of the atom

Bohr Model (planetary model) and its limitations



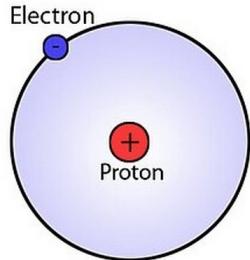
(a) Electronic emission transition



(b) Balmer series transitions

One-particle solutions to Schrodinger equation

Case 4: Hydrogen atom



Coulomb interaction between proton and electron

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right] \psi_n = E_n \psi_n$$

Take advantage of spherical symmetry → transform into spherical coordinates

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Make an ansatz → separation of variables of the radial and angular components

$$\Psi_{nlm}(r, \theta, \phi) = R_{n,l}(r)Y_{lm}(\theta, \phi)$$

Can solve for the wavefunctions analytically!

One-particle solutions to Schrodinger equation

Case 4: Hydrogen atom

$$\Psi_{nlm}(r, \theta, \phi) = R_{n,l}(r)Y_{lm}(\theta, \phi)$$

$$E_n = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2}$$

Each wavefunction is uniquely characterized by three quantum numbers, n , l , and m
Quantum numbers \leftrightarrow conserved quantities

n is the principle quantum number: 1, 2, 3, ...

\rightarrow energy, electron shell

l is the azimuthal quantum number: 0, 1, 2, ... $n - 1$

\rightarrow orbital angular momentum

m is the magnetic quantum number: $-l, \dots, l$

\rightarrow sub-orbital angular momentum

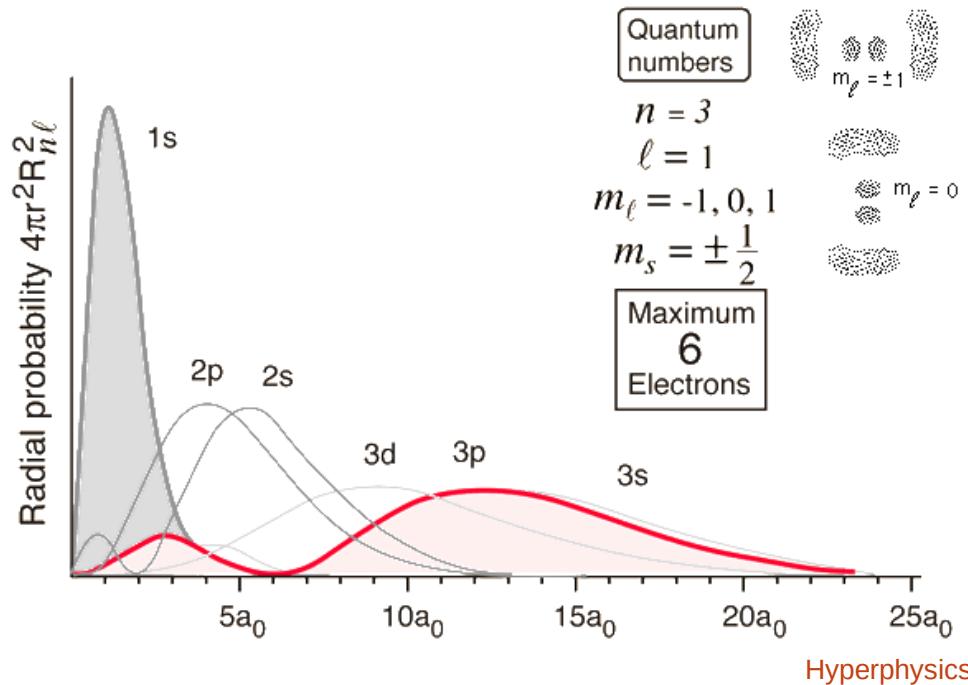
and spin m_s : $+1/2, -1/2$

One-particle solutions to Schrodinger equation

Case 4: Hydrogen atom

$$\Psi_{nlm}(r, \theta, \phi) = \underline{R_{n,l}(r)} Y_{lm}(\theta, \phi)$$

$$E_n = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2}$$



One-particle solutions to Schrodinger equation

Case 4: Hydrogen atom

$$\Psi_{nlm}(r, \theta, \phi) = \underline{R_{n,l}(r)} Y_{lm}(\theta, \phi)$$

$$E_n = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2}$$

n=1,2 n=3
 Separated
 Combined

n	ℓ	m_ℓ	$F(\phi)$	$P(\theta)$	$R(r)$
3	0	0	3s	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$
3	1	0	3p	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$
3	1	± 1	3p	$\frac{1}{\sqrt{2\pi}} e^{i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$
3	2	0	3d	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3\cos^2\theta - 1)$
3	2	± 1	3d	$\frac{1}{\sqrt{2\pi}} e^{i\phi}$	$\frac{\sqrt{15}}{2} \sin\theta \cos\theta$
3	2	± 2	3d	$\frac{1}{\sqrt{2\pi}} e^{i2\phi}$	$\frac{\sqrt{15}}{4} \sin^2\theta$

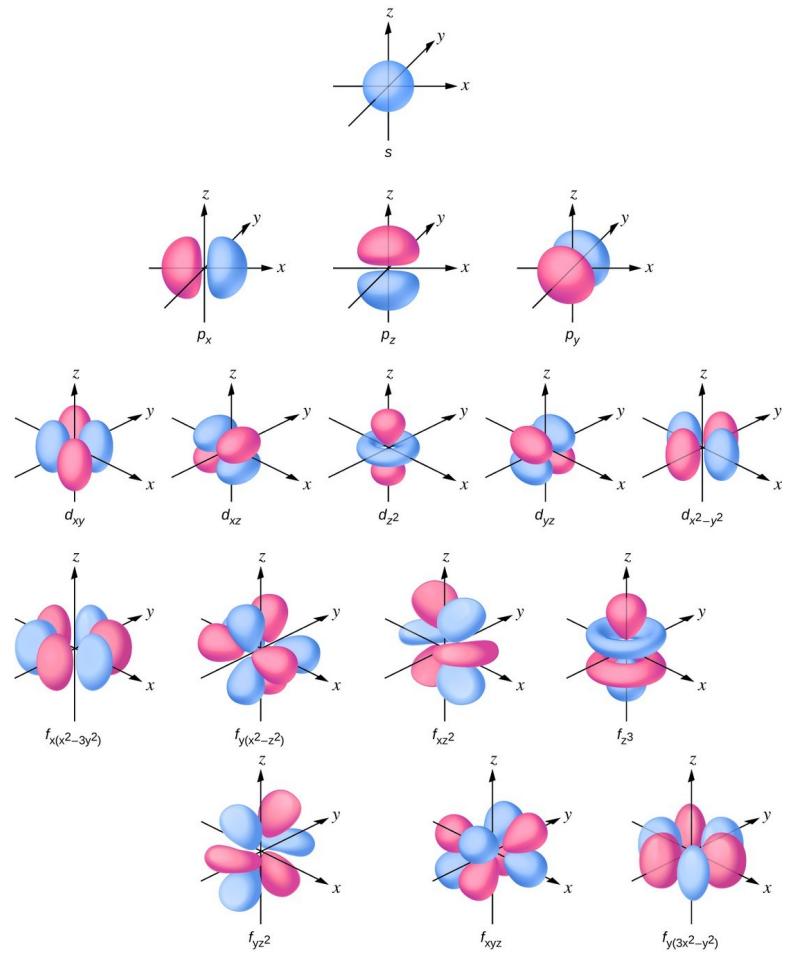
$$a_0 = \frac{\hbar^2}{me^2} = 0.0529 \text{ nm} = \text{first Bohr radius}$$

One-particle solutions to Schrodinger equation

Case 4: Hydrogen atom

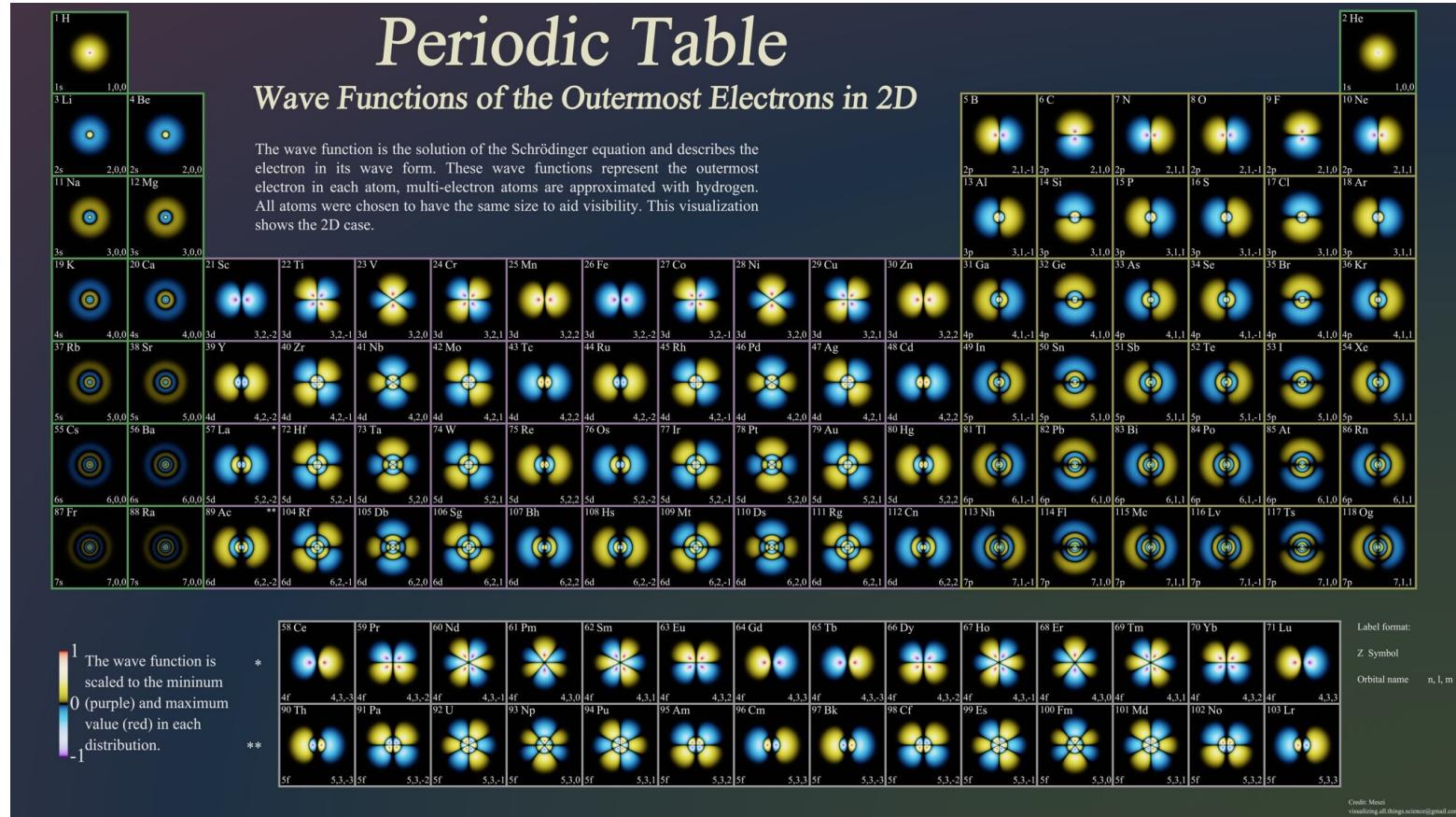
$$\Psi_{nlm}(r, \theta, \phi) = R_{n,l}(r)Y_{lm}(\theta, \phi)$$

	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$
$n=1$	1s	Forbidden combinations of quantum numbers				
$n=2$	2s	2p				
$n=3$	3s	3p	3d			
$n=4$	4s	4p	4d	4f		
$n=5$	5s	5p	5d	5f	5g	
$n=6$	6s	6p	6d	6f	6f	6h
$n=7$	7s	7p	7d	7f	7g	7h
$n=8$	8s	8p	8d	8f	8g	8h
	Allowed combinations of quantum numbers					



Structure of the atom

Spatial probability distribution of angular components of electron wavefunction in an isolated atom



One-particle solutions to Schrodinger equation

Case 4: Hydrogen atom

$$\Psi_{nlm}(r, \theta, \phi) = R_{n,l}(r)Y_{lm}(\theta, \phi)$$

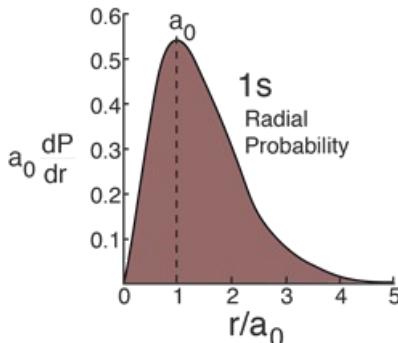
$$E_n = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2}$$

Each unique quantum state has a unique $n/l/m$

Orbitals of the same n but different l and m are “energetically degenerate”

Bohr radius $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m}$

Most probable distance of electron
in ground state of hydrogen



The hydrogen atom provides the basis for the entire chemical alphabet and the basis for chemical intuition about materials

Summary: one-particle solutions to Schrodinger equation

$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \psi(x) = E\psi(x)$$

Case 1: Free particle (1D)

Case 2: Free particle in a box (1D)

Case 3: Quantum HO

Case 4: Hydrogen atom

QM Notation: operators and expectation values

For each observable, there is a *Hermitian* (i.e., real-valued) *operator*
Measurement of an **observable** yields the eigenvalue of that operator

$$\hat{A}\phi(r) = a\phi(r)$$

Examples

Energy $\hat{H}\psi = E\psi$
$$\hat{H}\psi = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right] \psi(x) = E\psi(x)$$

Momentum $\hat{p}_x\phi(x) = -i\hbar \frac{\partial}{\partial x} \phi(x)$

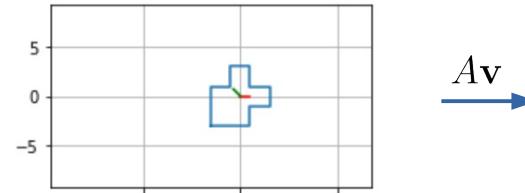
Kinetic Energy $\hat{T}\phi(x) = \frac{\hat{p}_x \cdot \hat{p}_x}{2m} \phi(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \phi(x)$

Linear algebra: eigenvalues and eigenvectors

Eigenvector = characteristic vector \mathbf{v} that is scaled by its eigenvalue upon linear transformation matrix A

$$A\mathbf{v} = \lambda\mathbf{v}$$

'eigen' = German for 'own'



In QM, eigenvectors or eigenstates are called "stationary states", because the position probability density does not depend on time

$$\hat{H}\psi = E\psi$$

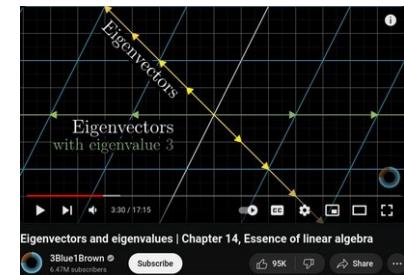
$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$$

$$\rho(r, t) = |\Psi(r, t)|^2 = \Psi^*\Psi = \rho(r)$$

Only need to solve for the time-independent (position) $\psi(x)$

Can construct the time-dependent solution from eigenvalues (allowed energy levels) and eigenfunctions (wavefunctions)

A nice graphical refresher from 3Blue1Brown



QM Notation: operators and expectation values

Expectation values (averages)

The expectation value of a quantity (e.g., energy, position, momentum) is determined by the corresponding operator

$$\langle a \rangle = \int \psi^* \hat{A} \psi dr$$

QM Notation: operators and expectation values

Expectation values (averages)

The expectation value of a quantity (e.g., energy, position, momentum) is determined by the corresponding operator

$$\langle a \rangle = \int \psi^* \hat{A} \psi dr$$

$$\int \psi_i^* \left[-\frac{\hbar^2}{2m} \nabla^2 + U \right] \psi_i dr = \langle \psi_i | \hat{H} | \psi_i \rangle = E_i$$

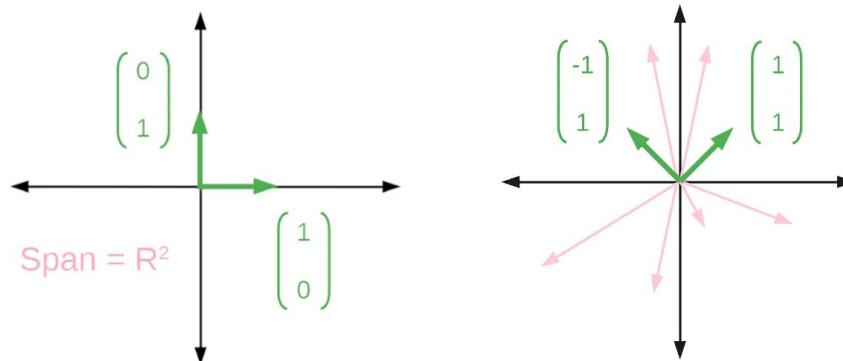
Bra-ket notation

$$\psi = \psi(r) = |\psi\rangle$$

$$\int dr \psi_i^*(r) \psi_j(r) = \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

Linear algebra: Basis sets

Familiar examples:



Orthonormality

$$\vec{a}_i \cdot \vec{a}_j = \delta_{ij}$$

Basis vectors:

- Linearly independent
- Span the vector space

Write any vector within a vector space as a linear combination of the basis vectors

Matrix formalism of QM

To implement QM in a computer, need to discretize the problem into a numerical solution

Functional form $\hat{H}\psi = E\psi$

Vector/matrix form $\hat{H}|\psi\rangle = E|\psi\rangle$

Expand a wavefunction as a linear combination of basis vectors

$$|\psi\rangle = \sum_{n=1,\dots,k} c_n |\phi_n\rangle \quad \{|\phi_n\rangle\} \text{ k orthogonal basis functions}$$

e.g., plane waves, Gaussian functions

$$\begin{aligned} \langle \phi_m | \hat{H} | \psi \rangle &= E \langle \phi_m | \psi \rangle \\ &= E \sum_{n=1,\dots,k} c_n \langle \phi_m | \phi_n \rangle \\ &= E c_m \end{aligned}$$

Matrix formalism of QM

To implement QM in a computer, need to discretize the problem into a numerical solution

Matrix elements

$$\sum_{n=1,\dots,k} c_n \langle \phi_m | \hat{H} | \phi_n \rangle = E c_m$$

H_{mn}

Recast Hamiltonian operator as a matrix

$$\begin{pmatrix} H_{11} & \dots & H_{1k} \\ \vdots & & \vdots \\ H_{k1} & \dots & H_{kk} \end{pmatrix} \begin{pmatrix} c_1 \\ \vdots \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ \vdots \\ c_k \end{pmatrix}$$

Hamiltonian operator
is Hermitian
 $(H^*)^T = H$

Diagonalize to determine the eigenvalue and corresponding eigenvector

Functionals

A function of a function

$$F[f(x)] = y$$

Takes a function as input, outputs a number

Examples

Integrals $F[n(x)] = \int n(x)V(x)dx$

Expectation values $E[\psi] = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$

Functional derivative of an integral

$$\frac{\delta F[n(x)]}{dn(x)} = V(x)$$