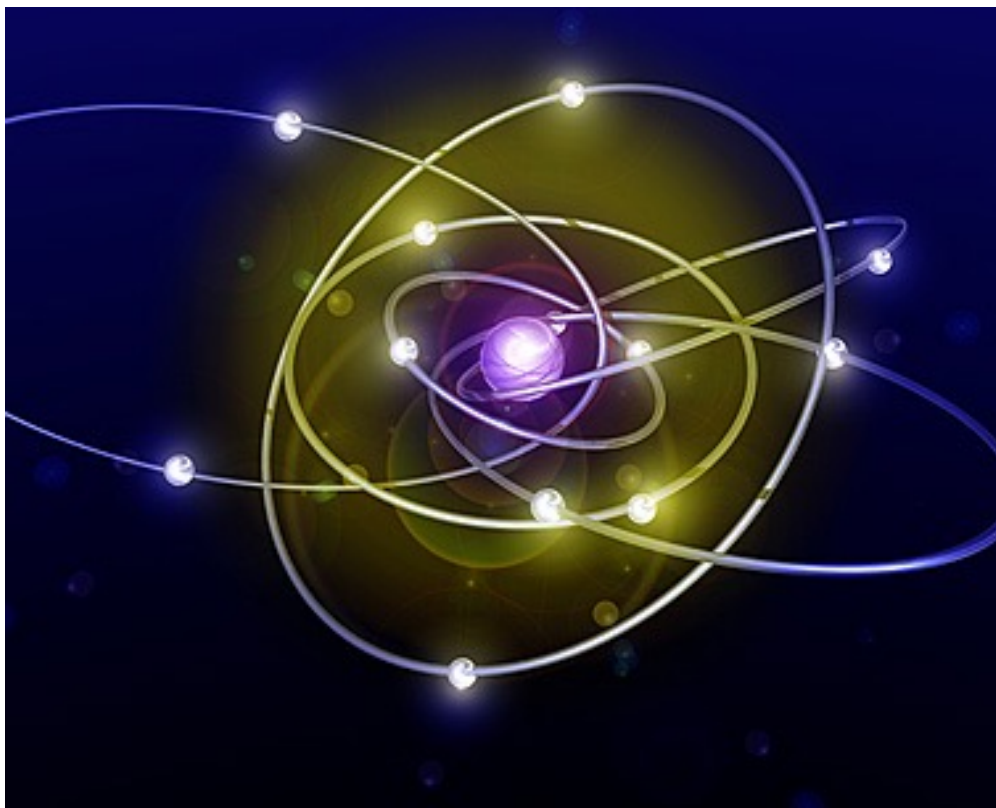# Intro to Quantum Mechanics and DFT

Niels Bohr:
"For those who are not shocked when they first come across quantum theory cannot possibly have understood it"

June 13, 2022 – Mississippi State

# Mike Janik background

Undergraduate – Yale University

Process Engineer for Procter and Gamble for 3 years

Graduate – University of Virginia

Joined Penn State in Fall 2006

Research – Atomistic modeling of catalysis, electrochemical systems
Classes taught: Thermodynamics, Mass Transfer, Reactor Design and Kinetics, Electrochemical Engineering, DFT Theory and Practice, Chemical Energy Tech.
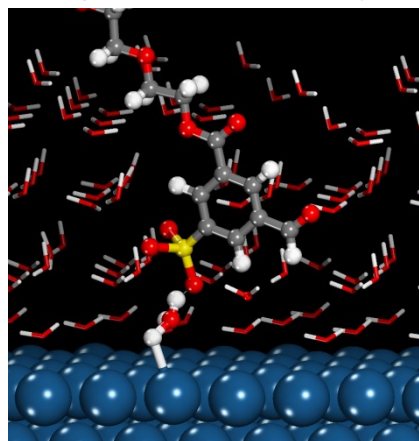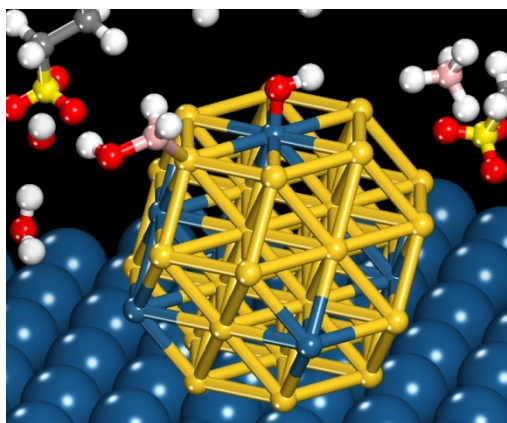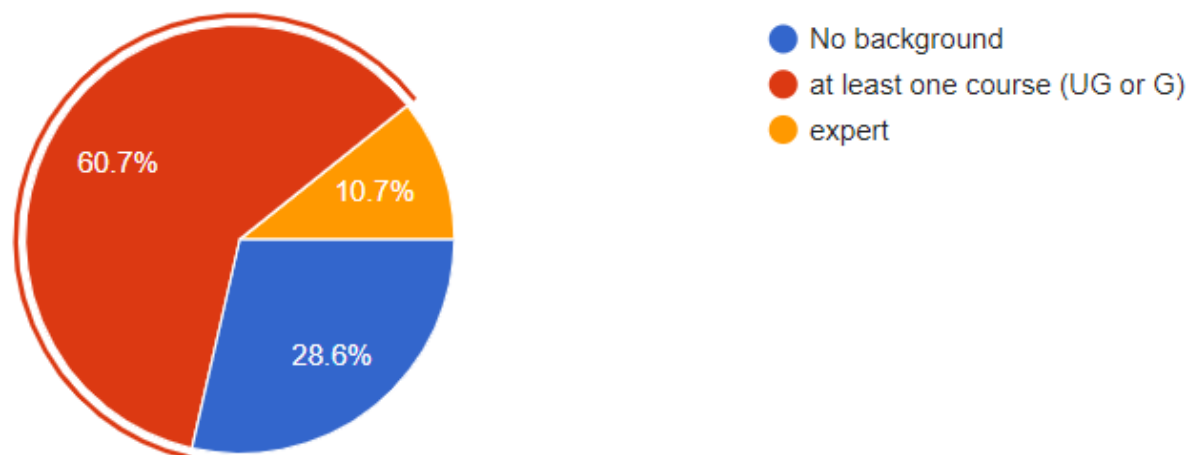
Family and Hobbies –
My wife Shannan and I have a 16 year old son Sam
and a 12 year old son Joseph

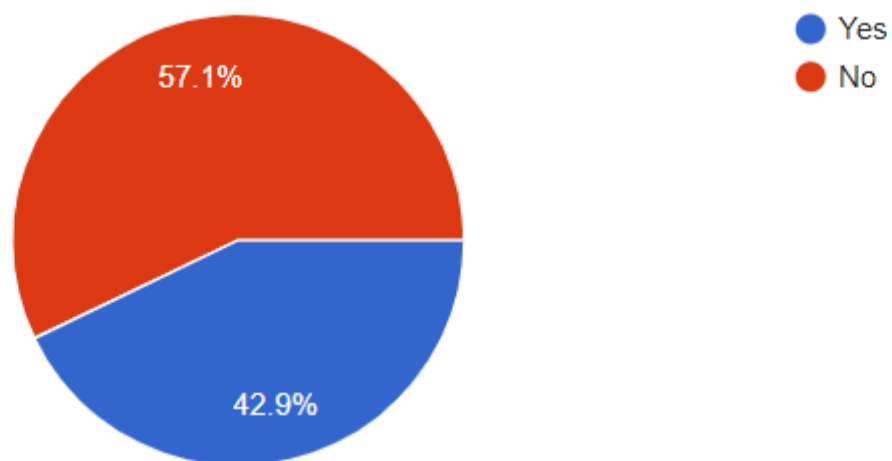# Your background – from Survey

Quantum mechanics background

28 responses

- No background
- at least one course (UG or G)
- expert

60.7%
10.7%
28.6%

Experience with any other electronic structure code

28 responses

- Yes
- No

57.1%
42.9%

Quantum Mechanics Basics – Our Objectives

Survey 1-1.5 semesters of QM in <50 minutes

Students should be able to:

Explain the general mathematical structure of quantum mechanics

Identify the major computational choices involved in using computational quantum mechanical methods

Apply computational quantum mechanics to a problem of interest

We will have to skip much of the math and breadth of methods, but will aim to meet the above objectives such that you can <u>comprehend research using computational quantum mechanical techniques</u> and <u>be intelligent users of available computational methods.</u>

I. Brief History of Quantum Mechanics Leading to the Schrodinger Equation

II. Time-Independent Schrodinger Equation, and the Postulates of QM

III. Particle in a Box – One Dimension, Single Particle Solution to Schrodinger Eqn.

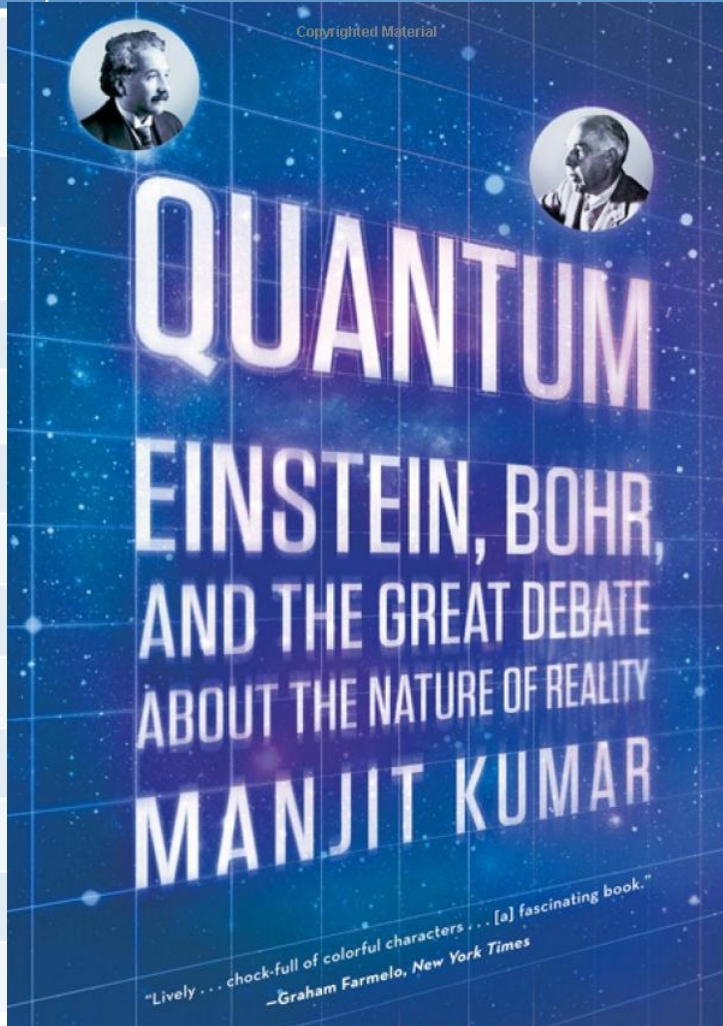IV. Hydrogen Atom – Determining Orbitals from Schrodinger Equation

I. Brief History of Quantum Mechanics Leading to the Schrodinger Equation

Why can't we just use F=ma to represent the physics of an electron?
What observations motivated development of the equations of quantum mechanics?

(we are going to race through the "history" slides after this one – they are there for reference)

Early History of Quantum Mechanics

When	Who	What
1898	Curie	
1901	Planck	
1905	Einstein	
1911	Rutherford	
1913	Bohr	
1922	Compton	
1922	Stern & Gerlach	
1924	Pauli	
1925	de Broglie	
1926	Schrödinger	
1927	Heisenberg	
1927	Davisson & Germer	
1927	Born	
1928	Dirac	

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QUANTUM

EINSTEIN, BOHR, AND THE GREAT DEBATE ABOUT THE NATURE OF REALITY

MANJIT KUMAR

"Lively . . . chock-full of colorful characters . . . [a] fascinating book."
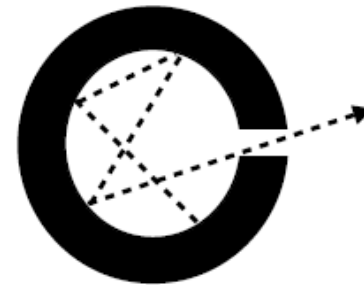—Graham Farmelo, New York Times

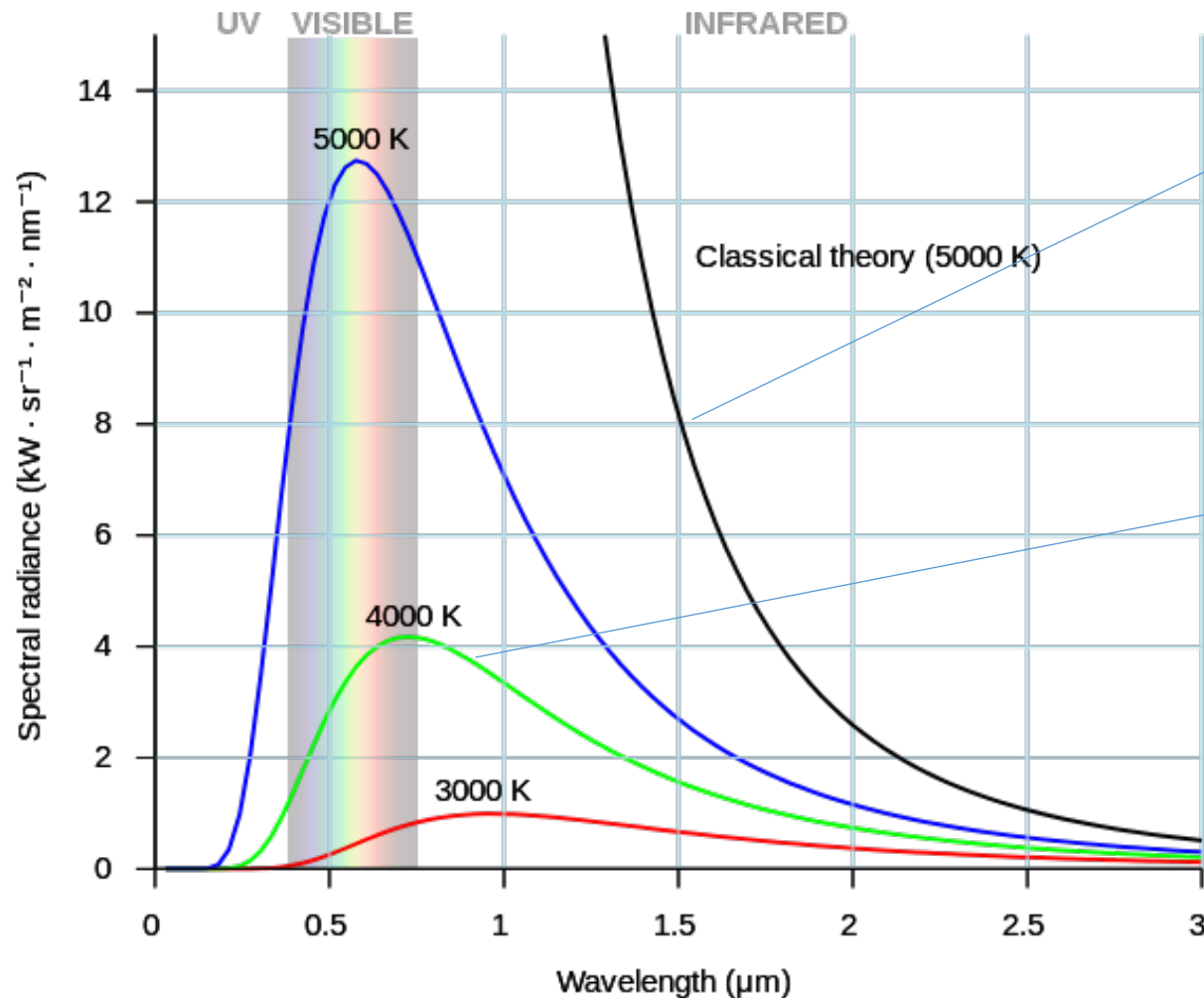# The limits of classical physics – the ultraviolet catastrophe

Max Planck (1858-1947)

All matter emits electromagnetic radiation (light) when its temperature is above absolute zero

A black-body is an ideal emitter, or an object that emit all wavelengths uniformly

Classical Theory Fails to Describe High Frequency Region of Blackbody Emission Spectrum

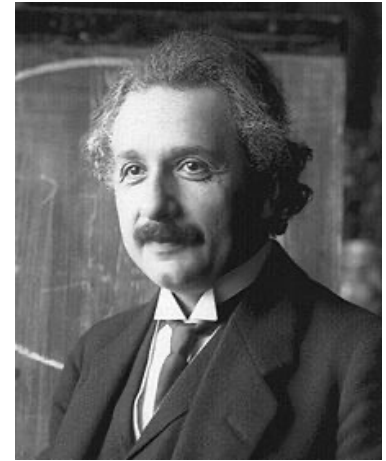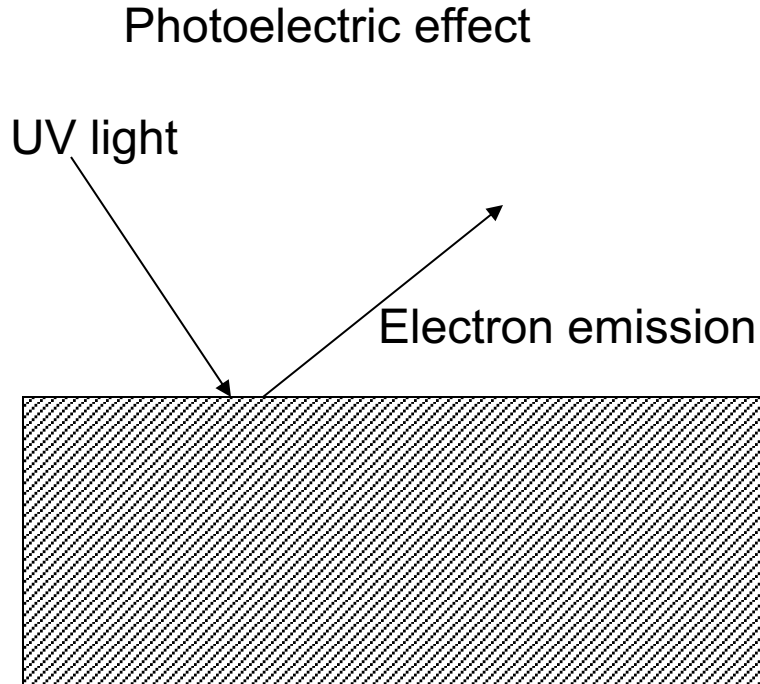$$B_\lambda(T) = \frac{2ckT}{\lambda^4},$$

$Prob(E) \sim exp(-E/k_bT)$

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

$$E = n \cdot \frac{hc}{\lambda} = n \cdot h\upsilon$$

Energy is restricted to integer multiples!

Explanation of Planck's correction: quantum nature of light

Photoelectric effect

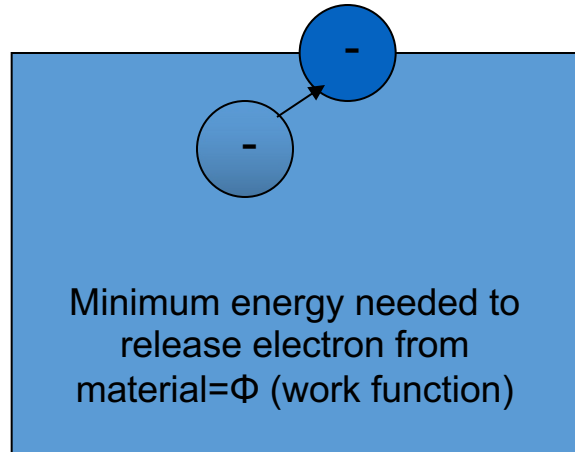UV light

Electron emission

Albert Einstein (1879-1955)

- Increase in light intensity **does not** increase the kinetic energy of the electrons
- Increase in light frequency **does** increase the electron kinetic energy

Einstein hypothesis for the photoelectric effect (1905)

Light; energy h*v

$E_{kin}=h*v-\Phi$

-

-

-

Minimum energy needed to release electron from material=Φ (work function)
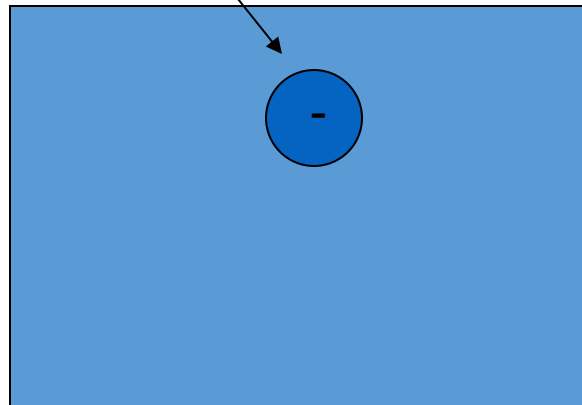
Electron in material

Electron on emission threshold
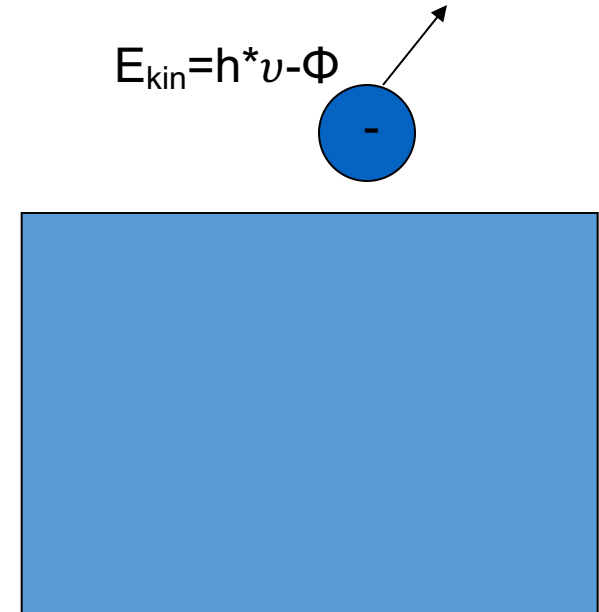
Emitted electron

-This hypothesis was confirmed by experiment; by comparison with experiment Einstein reproduced that h=6.626*10^{-34} Js/particle.
- This demonstrated that light does not always behave as a classical wave, but rather as a collection of particles (photons) with energies ε →
wave/particle duality
- Material can only accept energies in n*h*v packages → **quantization**

The Bohr atom and the de Broglie-hypothesis for matter waves

- Bohr hypothesis: Fixed Angular Momentum $L=m_e vr=n*h/2\pi$.

- Einstein hypothesis for photoelectric effect: wave/particle duality of light.

- de Broglie hypothesis: Matter also has a wave/particle duality; light (as in not heavy) particles (like electrons) have a significant wave character (1924 doctoral thesis).

- Explains the Bohr hypothesis; electrons can only occupy orbits that have a length that fits their wavelength

Louis de Broglie
(1892-1987)

r_2

Nucleus

r_1

electron

v

$\lambda_{electron}$

Orbit length=n*λ (n=2)
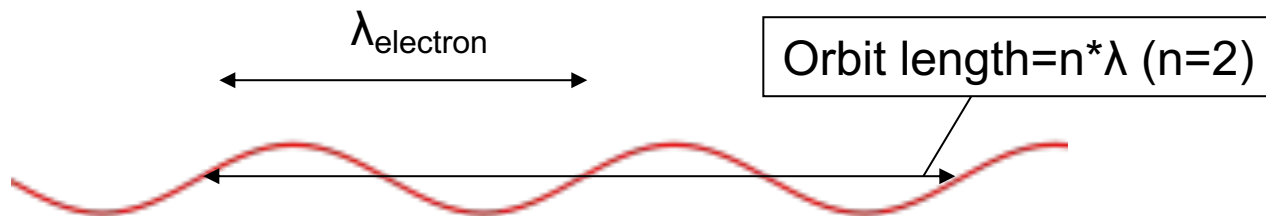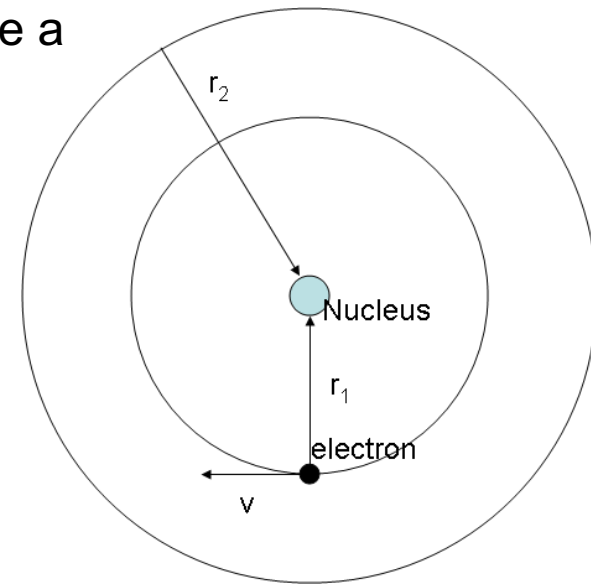
Wave-Particle Duality

We know from the work of Einstein that the energy of a photon is

$$E_p = h\nu = mc^2$$

Therefore its momentum is

$$p = mc = E_p/c = h\nu/c = h/\lambda$$

de Broglie then hypothesized that this was true for all matter

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

assigning wave character to all matter !

Prove for wave character of light and matter: Diffraction
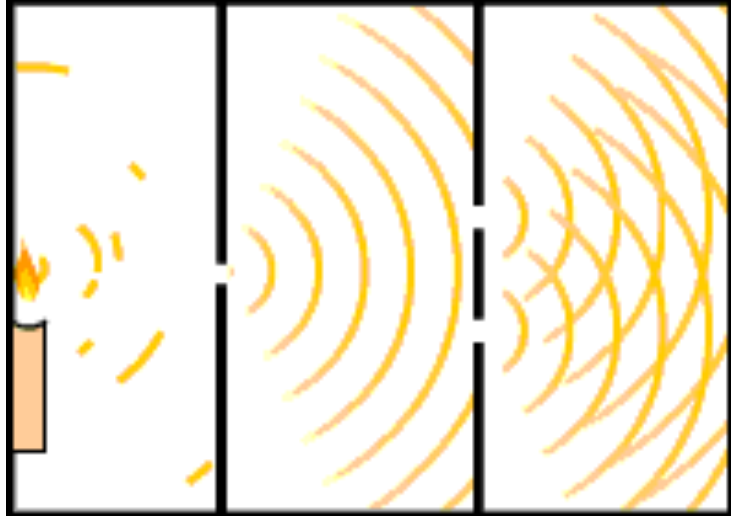
Interference pattern
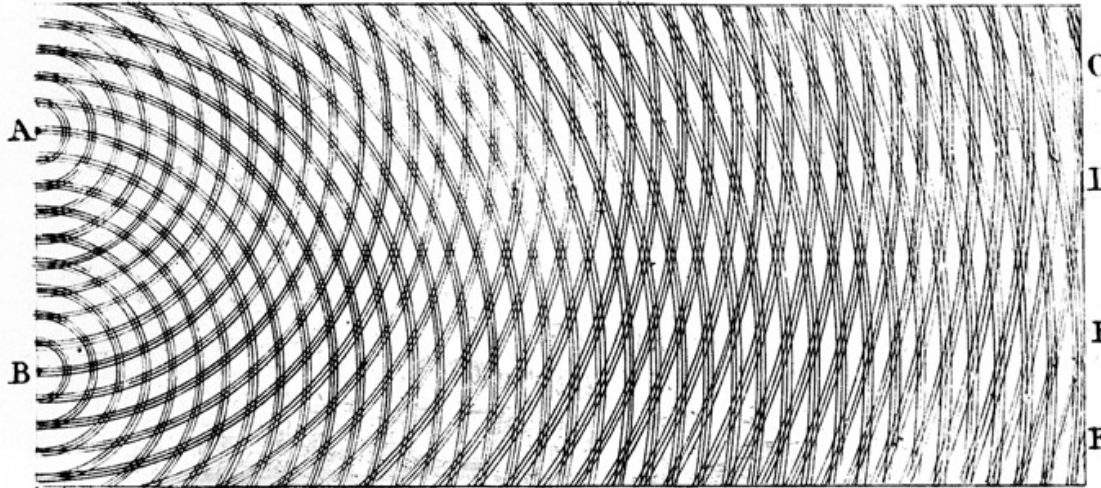
Light interference gives diffraction patterns (Thomas Young, 1803) indicating wave-character of light.

Electron Diffraction

Incident beams

Specimen

Objective lens

Diffraction pattern

Image
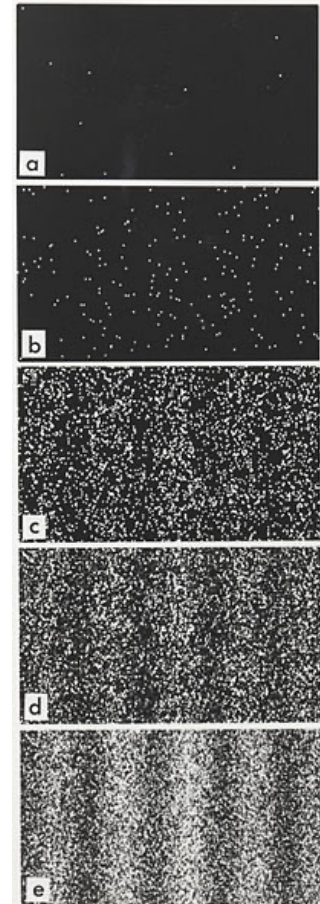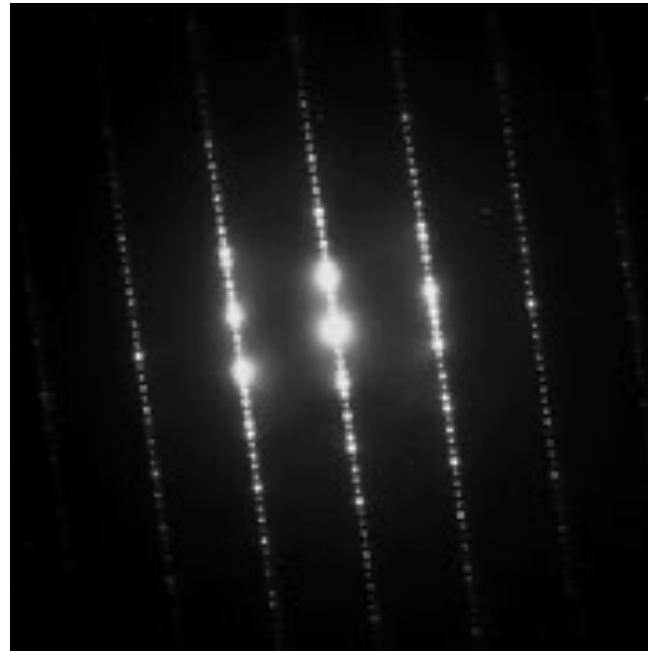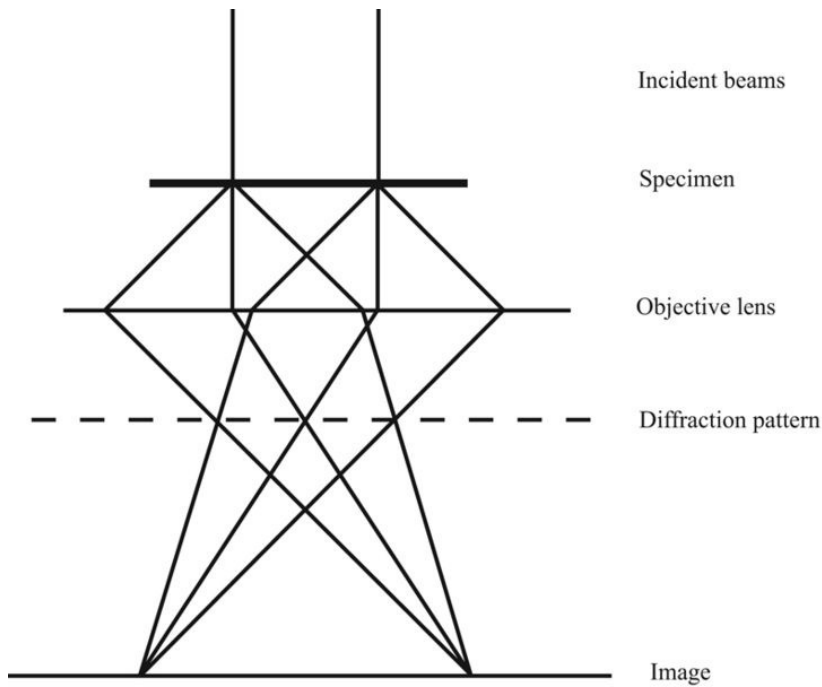
-The observation of electron diffraction confirmed the de Broglie hypothesis
- The de Broglie-wavelength of a particle signifies the relative importance of its wave and particle-nature

Transmission electron microscope electron diffraction pattern

George Thomson, Clinton Davisson and Lester Germer (1927)

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The Schrödinger equation: postulate that the states of an electron are the solution of a wave equation
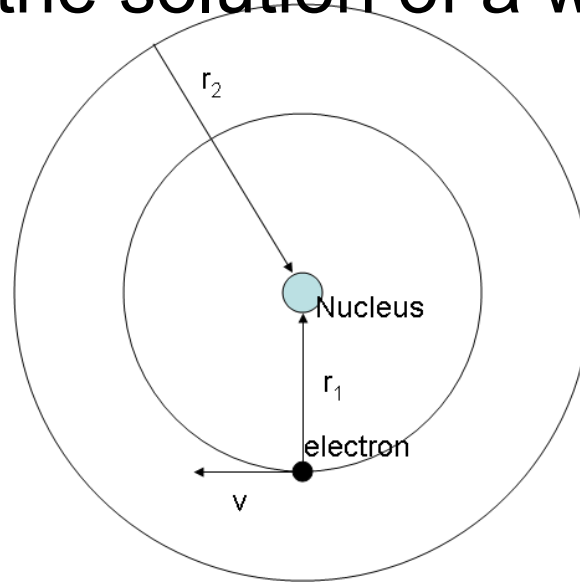
Erwin Schrödinger
(1887-1961)

- Electrons move in specific orbitals due to their partial wave-character (Bohr, de Broglie)

- As such, we might expect that we can model the behavior of events at the atomistic level using a wave-equation:

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial u(x,t)}{\partial t^2}$$

- In 1926 Erwin Schrödinger suggested that a wave equation Ψ could be used to describe matter waves:

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\,\Psi(x,t)$$

The postulates of Quantum Mechanics – the wavefunction is the state function of a quantum system

These postulates can not be proved; their proof is in the fact that they have resulted in a successful solution of real-world problems

I. The state of any quantum mechanical system can be specified by a function $\Psi(x,t)$, called the wave function of the system. The quantity $\Psi\Psi^*dx$ is the probability that the position x of the particle lies between x and Δx :

$$\text{Prob}(dx) = |\Psi(x,t)^2|\,dx$$

We refer to $|\Psi(x,t)^2|$ as the "density"

II. There exists some operator that can be used to determine any observable value of a system from the wavefunction

$$\hat{O}\,\Psi = O\,\Psi$$
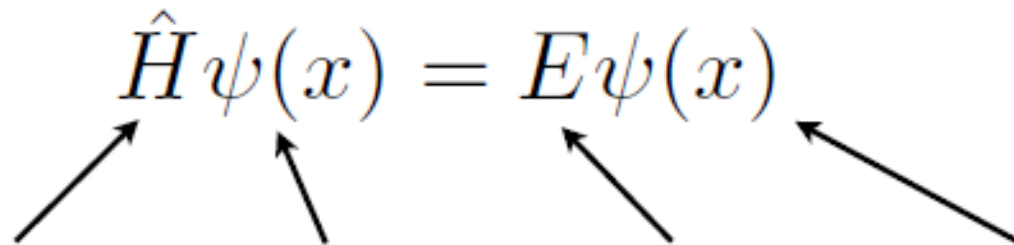
III. The observable variable is given by:

$$<A> = \frac{\int \Psi \hat{A} \Psi^*}{\int \Psi \Psi^*}$$

→Weighted Average over all space

Schrodinger's equation looks like an energy balance (in operator language…)

The time-independent Schrödinger Equation

$$\hat{H}\psi(x) = E\psi(x)$$

Hamiltonian x Wave function = Energy x Wave function

Hamiltonian operator – the set of mathematical operations that need to be done to the wavefunction to return the energy times the wavefunction

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

.

Kinetic Energy   +   Potential Energy   =   Total Energy

Need V(x) function, rewrite in 3d…..

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Particle in a (one dimensional) box – a simple physical system that illustrates the consequences of a quantum treatment
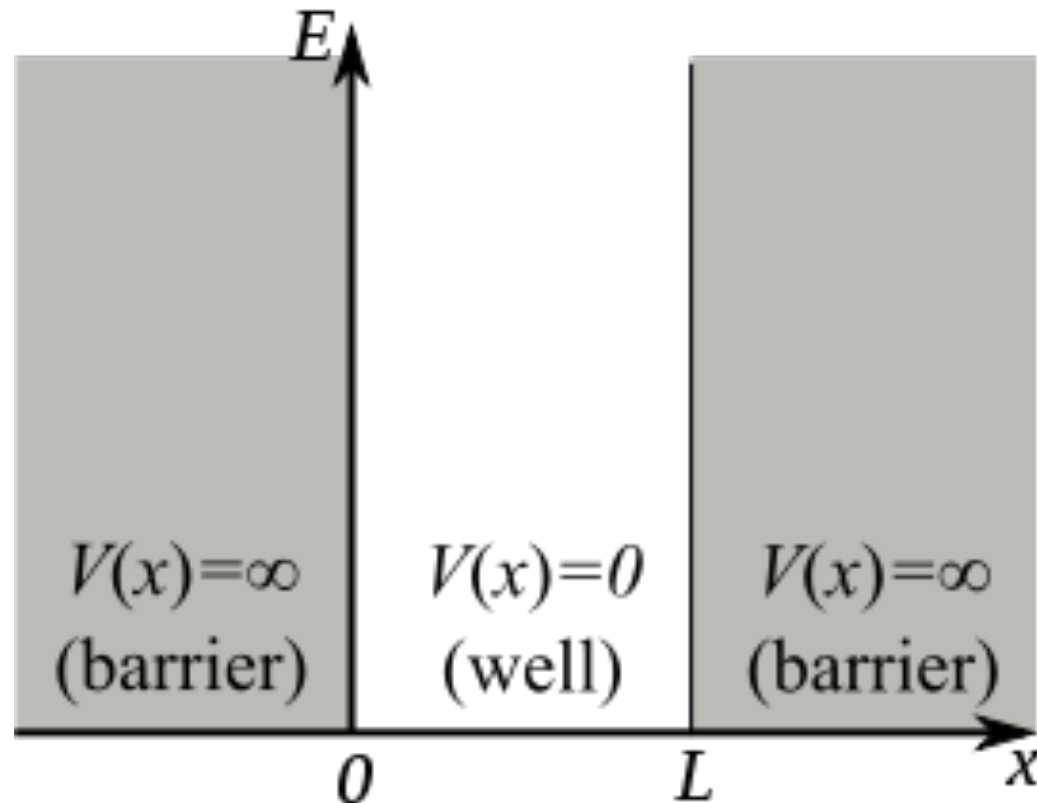
$$\frac{-\hbar^2}{2m}\frac{d}{dx^2}\psi(x) + V(x)\,\psi(x) = E\psi(x)$$

Solve for ψ and E (time probably won't allow – consequences key on next slides)

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

Particle in a box – Energy and wavefunctions

$$\psi_n(x \quad) = \begin{cases} A\sin(k_n x) & , \quad 0 < x < L, \\ 0, & \text{otherwise,} \end{cases}$$

$$k_n = \frac{n\pi}{L}, \quad \text{where} \quad n = \{1, 2, 3, 4, \ldots\},$$

E   ψ   n $|\psi|^2$

6
5
4
3
2
1

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2} = \frac{n^2 h^2}{8mL^2}$$

Last slide has the mathematical solutions to a particle in a box

What is "shocking" from the solutions of the particle in a box problem?

There are "nodes" -places where the wavefunction = 0
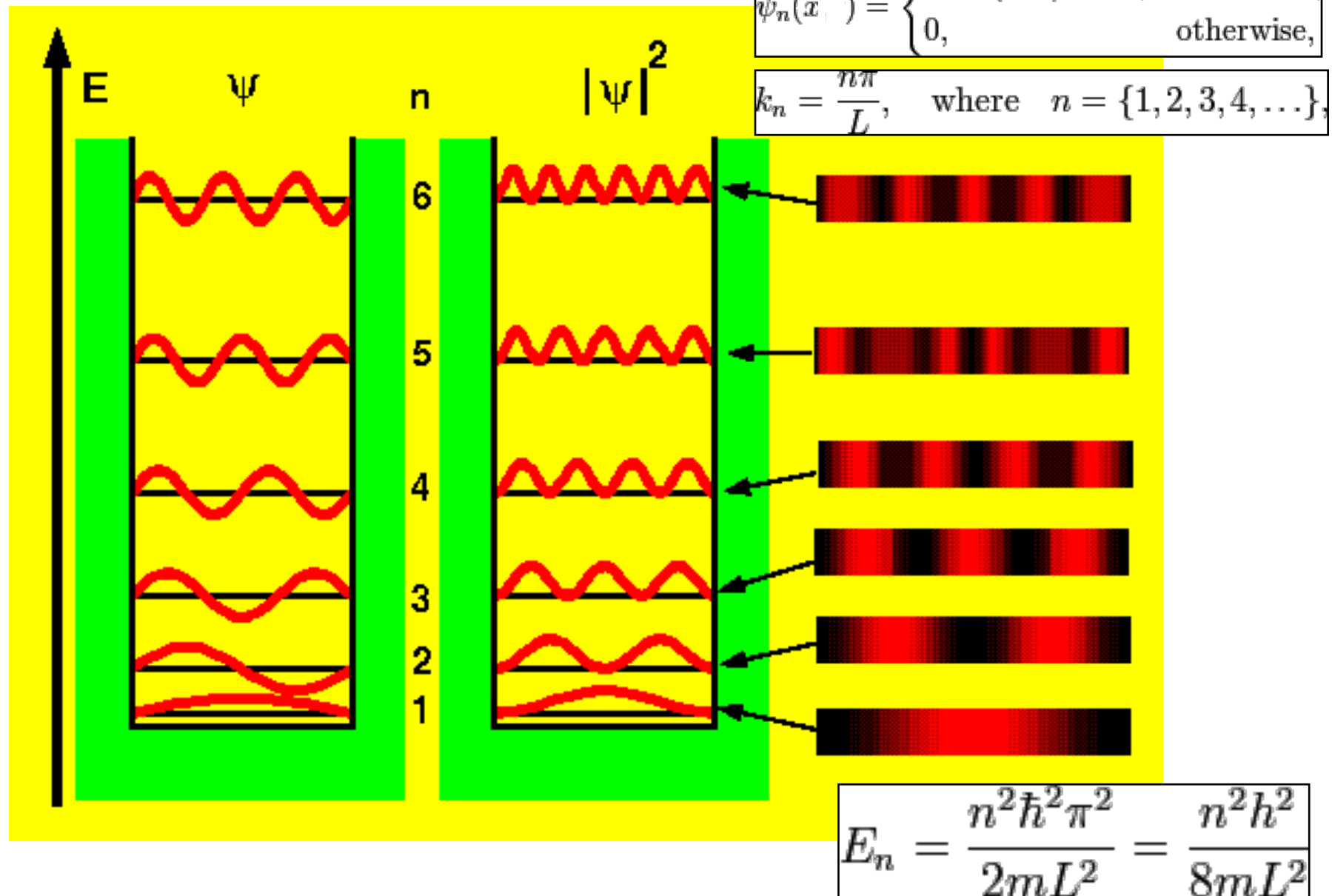
Last slide has the mathematical solutions to a particle in a box

Niels Bohr:
"For those who are not shocked when they first come across quantum theory cannot possibly have understood it"

What is "shocking" from the solutions of the particle in a box problem?

1) Energy levels are quantized! We can not give the particle any energy we want
2) The wavefunction has nodes! In level 2, 50% chance particle is on left side, 50% chance it is on right side, but 0% chance it ever exists at the exact middle.
3) Zero point energy – there is no "0" state of rest, the ground state still has energy and moves

Quantum to Classical Transition

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2} = \frac{n^2 h^2}{8mL^2} \qquad \Delta E(n_1 \to n_2) = (n_2{}^2 - n_1{}^2) \frac{h^2}{8mL^2}$$

Electron in a 1 angstrom box:

$$\Delta E(n_1 \to n_2) = (2^2 - 1^2) \frac{(6.626 x 10^{-34})^2}{8(9.11 x 10^{-31}) (10^{-10})^2 (1.6 x 10^{-19})} = 4.52 \text{ eV}$$

Electron in a 1 meter box:

$$\Delta E(n_1 \to n_2) = (2^2 - 1^2) \frac{(6.626 x 10^{-34})^2}{8(9.11 x 10^{-31}) 1^2 (1.6 x 10^{-19})} = 1.13 x 10^{-18} \text{ eV}$$

Baseball in a 1 meter box:

$$\Delta E(n_1 \to n_2) = (2^2 - 1^2) \frac{(6.626 x 10^{-34})^2}{8(0.15) 1^2 (1.6 x 10^{-19})} = 6.86 x 10^{-48} \text{ eV}$$

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The Hydrogen Atom – now we add the nucleus-electron Coulomb as the V term. Equation is still analytically solvable

V(r) – from Coulomb's law, gives a one particle, central force problem

$$\frac{-\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{r}\psi = E\psi$$

Z = positive charge on nuclei (1 for hydrogen), *e* = elementary charge, *r* = distance from the nuclei

Convert to spherical coordinates, "2 or 3 chapters of math" and can show:

$$\psi = R(r)Y^m{}_l(\theta, \phi)$$

$$\frac{1}{R}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \frac{2\mu}{\hbar^2}(Er^2 + ke^2 r) = l(l+1)$$

where the radial solution is multiplied by the spherical harmonics (eigenfunctions of the square of the magnitude of the orbital angular momentum of a single particle)

The Hydrogen Atom – Radial functionals all exponentially decay with respect to distance from nucleus (r)

$$E_n = \frac{-me^4}{8\varepsilon_0^2 h^2} \frac{1}{n^2} = \frac{-13.6eV}{n^2} \quad n = 1,2,3,...$$

R(r) =

n=1

$$2 \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

solutions only for l=1
(s orbitals)

n=2

$$\left(\frac{1}{2a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

solutions for l=0,1
(s, p)

n=3 $$2 \left(\frac{1}{3a_0}\right)^{3/2} \left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}(r/a_0)^2\right) e^{-r/3a_0}$$

solutions for l=0,1,2   (s, p, d)

The Hydrogen Atom – Radial wavefunctions all exponentially decay with respect to distance from nucleus (r)

n=1

s $\quad 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

r/a0

n=2

2s

2p   R21

R20

r/a0

n=3

3s   3p

R31

R32   3d

R30
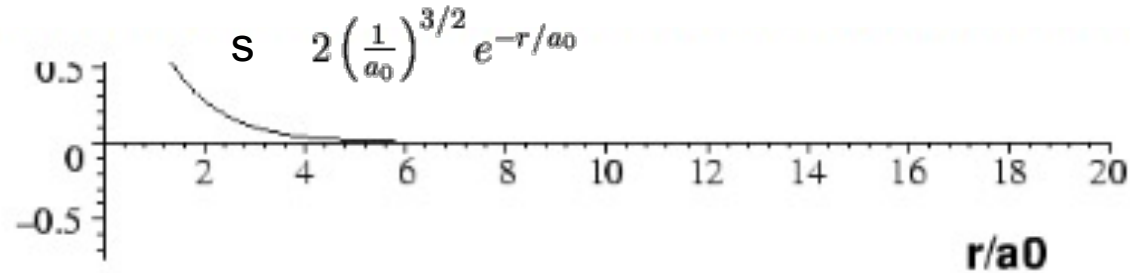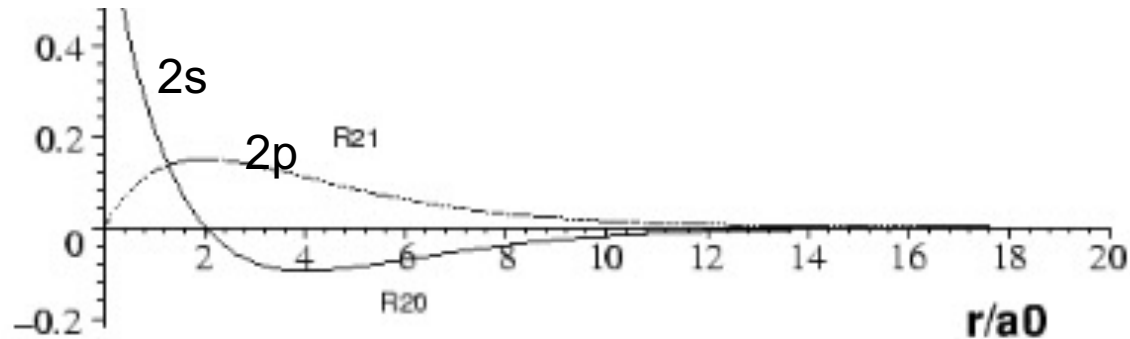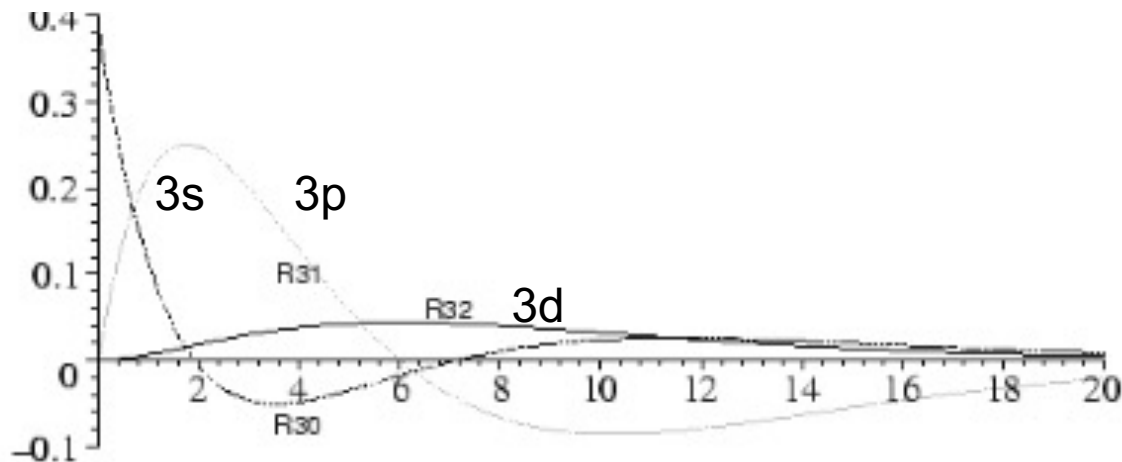
The Hydrogen Atom – Radial Distribution Functions

Probability of finding the electron a given distance from the nuclei

$$prob(0, r') = \int_{0}^{r'} |R_{nl}(r)|^2 r^2 \, dr \; *$$

$$\iint |Y_l^m(\phi, \theta)|^2 sin\theta \, d\theta d\phi$$

Fig. (C)

Probability density $= r^2|R_{nl}(r)|^2$

Ground state
$n = 1$
$l = 0$

Dashed line : Radius by Bohr's quantum theory

$n = 2$
$l = 0$

$n = 2$
$l = 1$

$n = 3$
$l = 0$

$n = 3$
$l = 1$

$n = 3$
$l = 2$

r / a_0 (a_0 : Bohr radius)
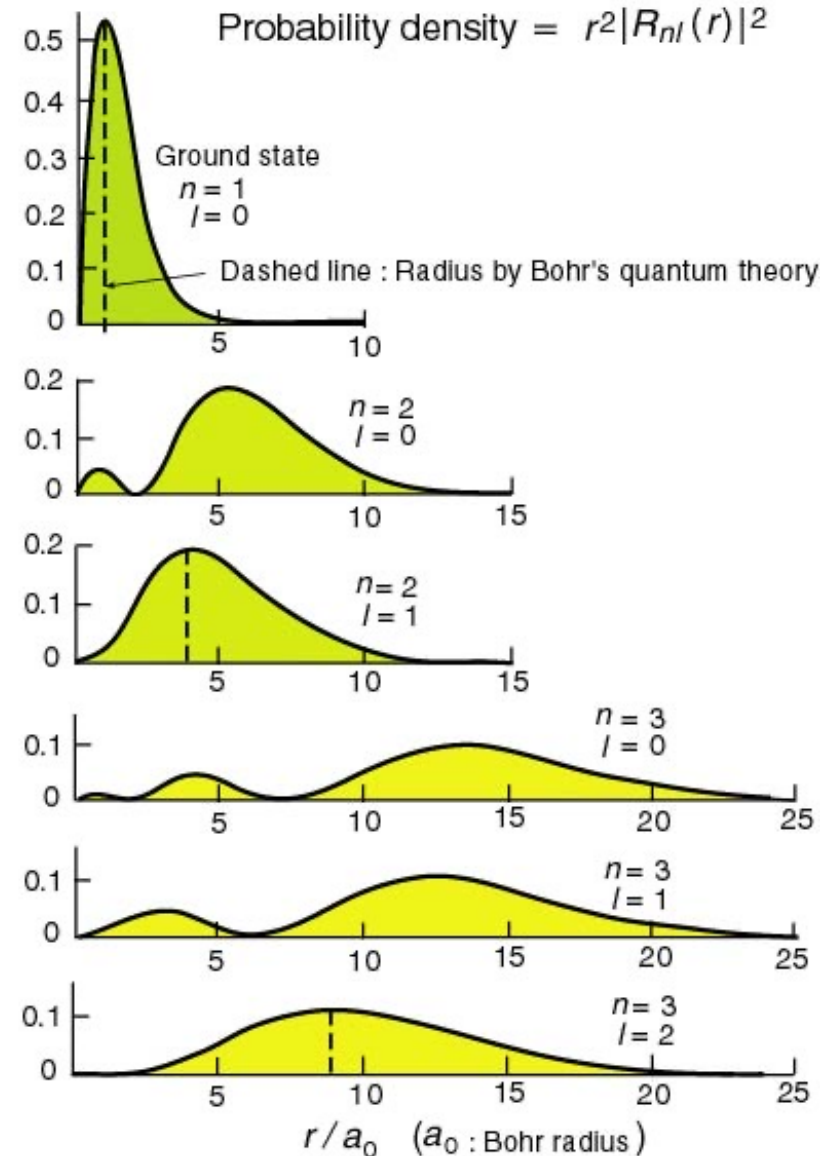
The Hydrogen Atom – Spherical Harmonics part of solution

l = 0, 1, 2, …
m = -*l*, …, 0, …,*l*

l = s, p, d, f
m = p_x, p_y, p_z
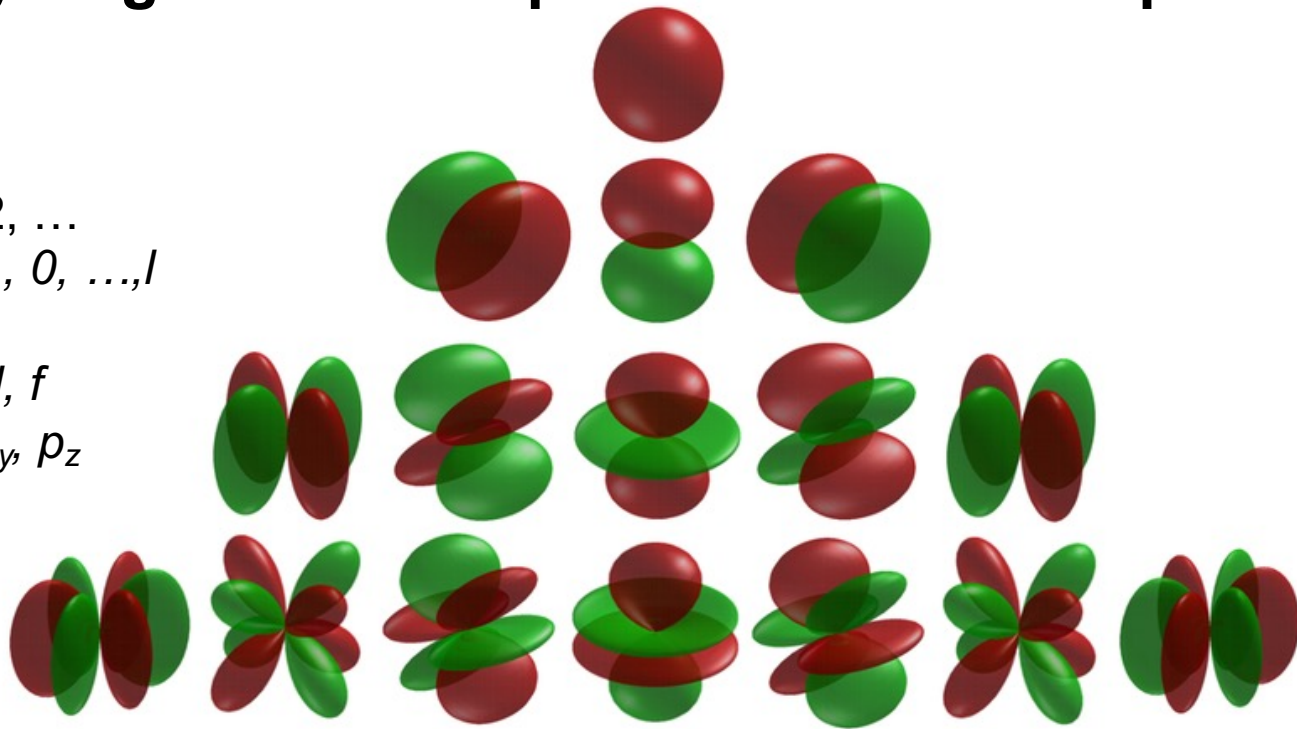
$$Y_0^0(\theta, \varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}$$

$$Y_1^{-1}(\theta, \varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta\, e^{-i\varphi}$$

$$Y_1^0(\theta, \varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta$$

$$Y_1^1(\theta, \varphi) = \frac{-1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta\, e^{i\varphi}$$

$$Y_2^{-2}(\theta, \varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2\theta\, e^{-2i\varphi}$$

$$Y_2^{-1}(\theta, \varphi) = \frac{1}{2}\sqrt{\frac{15}{2\pi}} \sin\theta\, \cos\theta\, e^{-i\varphi}$$

$$Y_2^0(\theta, \varphi) = \frac{1}{4}\sqrt{\frac{5}{\pi}} (3\cos^2\theta - 1)$$

$$Y_2^1(\theta, \varphi) = \frac{-1}{2}\sqrt{\frac{15}{2\pi}} \sin\theta\, \cos\theta\, e^{i\varphi}$$

$$Y_2^2(\theta, \varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}} \sin^2\theta\, e^{2i\varphi}$$

The Hydrogen Atom – spherical harmonic x radial
These are analytical, spatial functions ($\psi(x,y,z)$ or $\psi(r,\theta,\phi)$)

			Table 1: Wave functions and their components		
n	ℓ	m	$R_{n\ell}$	$Y_{\ell m}$	$\psi_{n\ell m} = R_{n\ell} Y_{\ell m}$
1	0	0	$2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$
2	0	0	$\left(\frac{1}{2a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$
2	1	±1	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-r/2a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$	$\frac{1}{8}\sqrt{\frac{1}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin\theta e^{\pm i\phi}$
3	0	0	$2\left(\frac{1}{3a_0}\right)^{3/2}\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}(r/a_0)^2\right)e^{-r/3a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(27 - 18\frac{r}{a_0} + 2(r/a_0)^2\right)e^{-r/3a_0}$
3	1	0	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\left(1 - \frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\cos\theta$
3	1	±1	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\left(1 - \frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$	$\frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$
3	2	0	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$	$\frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}(3\cos^2\theta - 1)$
3	2	±1	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$	$\pm\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{\pm i\phi}$	$\frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}\sin\theta\cos\theta e^{\pm i\phi}$
3	2	±2	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2i\phi}$	$\frac{1}{162\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}\sin^2\theta e^{\pm 2i\phi}$

$\${1\over 81}\sqrt{2\over \pi}$ - ${r\over a\_0}\right){r$

Key point for QM basics:

Schrodinger's equation is a **differential equation on the "wavefunction"** with eigenvalues giving the energy for each wavefunction

The "**wavefunction" embeds all state information of the electron**, but itself doesn't have a physical meaning

Squaring the wavefunction gives the probability of finding an electron as a function of position

Though not the easiest differential equation to solve, solving Schrodinger's equation for the H atom gives 1s, 2s, 2p, 3s, 3p, 3d, … functions. **H wavefunctions are functions of space (x, y, z or r, θ, ϕ)**

More than 1 electron: He atom Schrodinger Equation – not analytically solvable

$$H\psi(\vec{r}_1, \vec{r}_2) = \left[\sum_{i=1,2} \left(-\frac{\hbar^2}{2\mu}\nabla^2_{r_i} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) - \frac{\hbar^2}{M}\nabla_{r1} \cdot \nabla_{r2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \psi(\vec{r}_1, \vec{r}_2)$$

KE electron   e – nucleus   KE nucleus   electron-electron

$$\mu = \frac{mM}{m+M} \qquad \vec{r}_1 \quad \vec{r}_2 \text{ Distance vectors between electron and nucleus)}$$

$$r_{12} = \left| \vec{r}_1 - \vec{r}_2 \right|$$

Heavy atoms: Born-Oppenheimer approximation, removes KE nucleus term. In atomic units (ie, non-dimensionalized by constants):

$$H\psi(\vec{r}_1, \vec{r}_2) = \left[-\frac{1}{2}\nabla^2_{r1} - \frac{1}{2}\nabla^2_{r2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right] \psi(\vec{r}_1, \vec{r}_2).$$

Wavefunction now a function of x_1, y_1, z_1, x_2, y_2, z_2 (or r_1, θ_1, ϕ_1, r_2, θ_2, ϕ_2).
Because of electron-electron term, this is not separable in any coordinate system.
Must be solved by approximate methods.

"Exchange" and "Correlation" arise in solving for a multi-electron wavefunction. These are non-classical…..
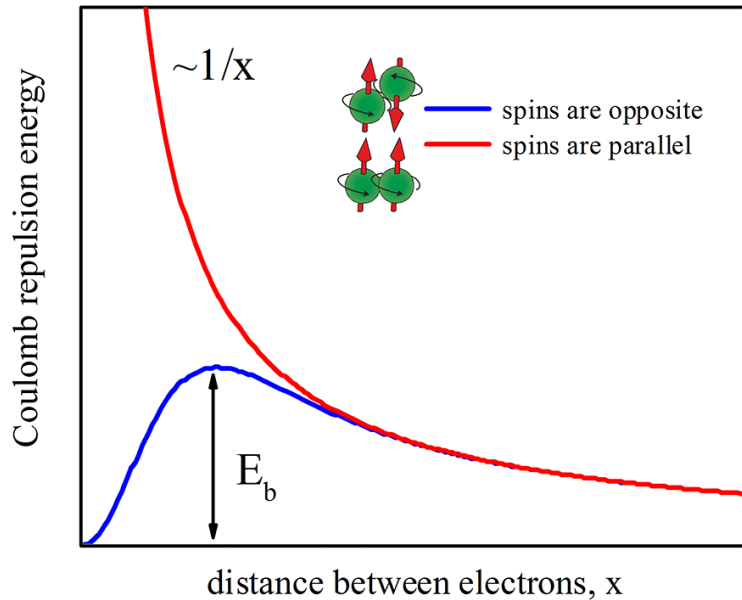
Exchange – an additional energy term that comes from a wavefunction needing to be antisymmetric with respect to changing which electron is which. Leads to "Pauli exclusion principle", and effectively raises energy beyond just e-e Coulomb repulsion

Correlation– an attractive interaction between electrons not captured by the average probability distribution, because electrons can "correlate" their motion. Important in all multi-electron systems, and the source of VDW interactions (ie, why Argon condenses…)
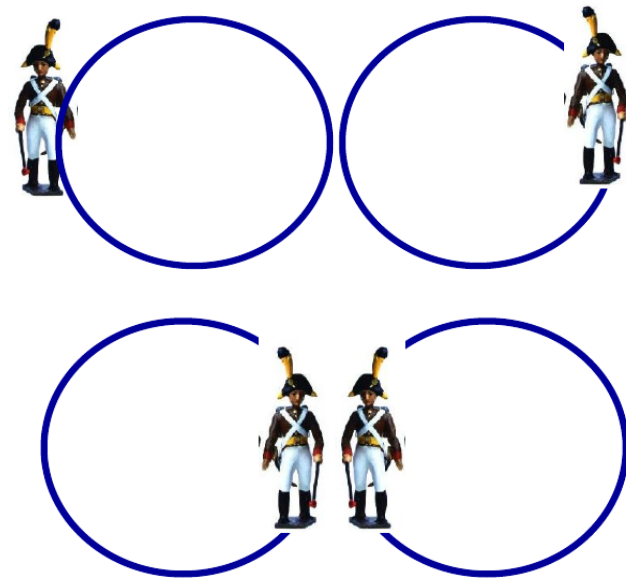
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Wavefunction now a function of x_1, y_1, z_1, x_2, y_2, z_2 (or r_1, θ_1, ϕ_1, r_2, θ_2, ϕ_2).
Because of electron-electron term, this is not separable in any coordinate system.
Must be solved by approximate methods.

Directions to take in finding an approximate solution for a multiple electron system:

"Wavefunction based" – we have the "right equation" but will need to find an approximate solution

"Density functional theory" – recast the problem to finding the total electron density rather than the set of wavefunctions

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

Try to write an equation for the total energy of the system using n(r) instead of wavefunctions. This isn't quite as a large a "reset" as it initially seems, but let's just review the underlying theory for now, afternoon we'll then talk about executing computationally.

- Given a potential, one obtains the wave functions via Schrödinger equation:

$$V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r})$$

The density is the probability distribution of the wave functions:

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

Thus

$$V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r}) \Rightarrow n(\mathbf{r})$$

Theorem

The potential, and hence also the total energy, is a unique functional of the electron density $n(\mathbf{r})$

Thus

$$V(\mathbf{r}) \Rightarrow \psi_i(\mathbf{r}) \Rightarrow n(\mathbf{r}) \Rightarrow V(\mathbf{r})$$

The electron density can be used to determine all properties of a system

"Orbital-free density functional theory" – great in theory, but not very useful because we don't know how to write the KE in terms of the density

Write all terms:

KE of electrons + electron-nuclear attraction + electron-electron repulsion

as functionals of the electron density $F(\rho(x,y,z)$ = a functional

Issue:
Neon atom:

KE = 128.9 au
Exchange = -12.1 au
Correlation = -0.4 au

The KE is large, and unknown how to write in terms of the density. Very sensitive to how this is written.

Orbital free DFT comes across like force-field development with a complex function

Kohn-Sham equations re-invoke the (non-interacting) wavefunction for the kinetic energy term. Discuss more tomorrow….

➢ Here are the Kohn-Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \hat{H}_{KS}\,\psi_i(\mathbf{r}) = \epsilon_i\,\psi_i(\mathbf{r})$$

$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}', \qquad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

$$n(\mathbf{r}) = \sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2.$$

➢ These equations describe not the true electrons in the system but the Kohn-Sham non-interacting electrons.

➢ The K-S electrons have their own orbitals ψ_i that will give us a ground state charge density that if the exchange correlation functional was exact will be not only the same ground state energy of the interacting electrons but it will also be the exact solution of the problem.

Kohn-Sham density functional theory basics

$$E[\{\psi_i\}] = 2\sum_i \int \psi_i \left[-\frac{\hbar^2}{2m} \right] \nabla^2 \psi_i \, d^3r + \int V_{\text{ion}}(\mathbf{r}) n(\mathbf{r}) d^3r + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r \, d^3r' + E_{XC}[n(\mathbf{r})] + E_{\text{ion}}(\{\mathbf{R}_I\}) \,,$$

electron kinetic energy   *electron nuclei Coulomb*   *electron electron "average" Coulomb*   *electron exchange +correlation*   *nuclei-nuclei Coulombic*

Kohn-Sham equations (Kohn and Sham, 1965):

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \,,$$

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'$$

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

The Kohn-Sham equations represent a mapping of the interacting many-electron system onto a system of noninteracting electrons moving in an effective potential due to all the other electrons. If the exchange-correlation energy functional were known exactly, then taking the functional derivative with respect to the density would produce an exchange-correlation potential that included the effects of exchange and correlation exactly.

Kohn-Sham density functional theory basics

$$E[\{\psi_i\}] = 2\sum_i \int \psi_i \left[-\frac{\hbar^2}{2m} \right] \nabla^2 \psi_i \, d^3r + \int V_{ion}(\mathbf{r})n(\mathbf{r}) d^3r + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r\, d^3r' + E_{XC}[n(\mathbf{r})] + E_{ion}(\{\mathbf{R}_I\}) ,$$

What does each term here represent?
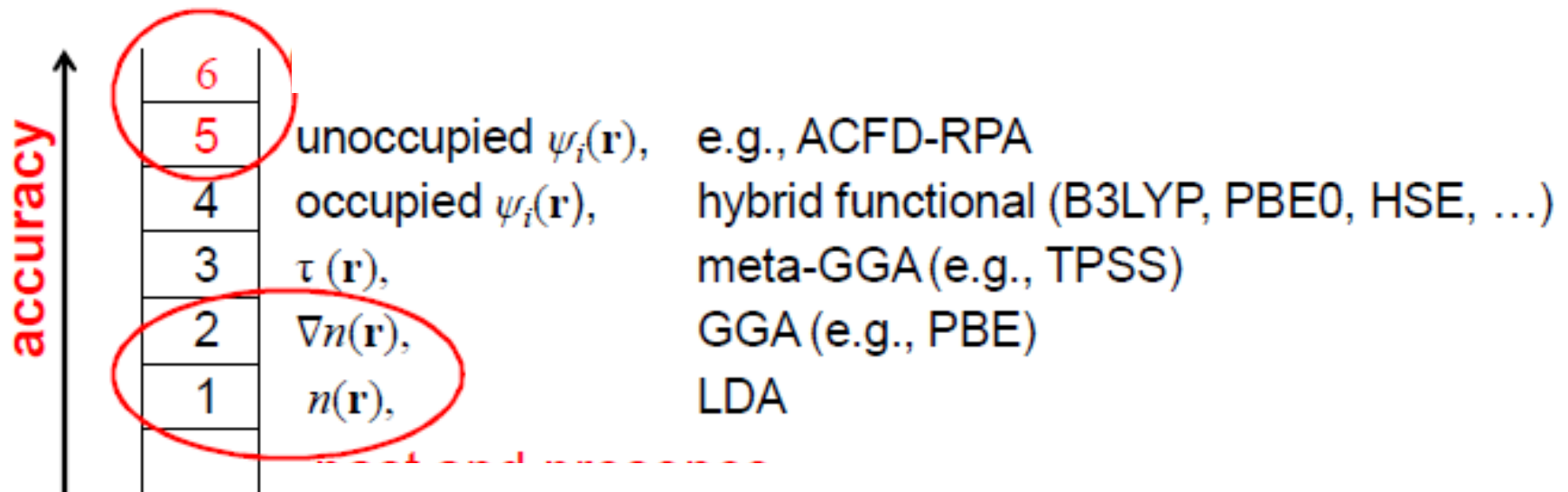
Kohn-Sham equations (Kohn and Sham, 1965):

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) ,$$

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'$$

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Exchange-Correlation Functionals

accuracy		
6		
5	unoccupied $\psi_i(\mathbf{r})$,	e.g., ACFD-RPA
4	occupied $\psi_i(\mathbf{r})$,	hybrid functional (B3LYP, PBE0, HSE, …)
3	$\tau(\mathbf{r})$,	meta-GGA (e.g., TPSS)
2	$\nabla n(\mathbf{r})$,	GGA (e.g., PBE)
1	$n(\mathbf{r})$,	LDA

$\tau(\mathbf{r})$:   Kohn-Sham kinetic energy density

ACFD :   adiabatic connection fluctuation dissipation
                theorem (Bohm, Pines (1953); Gell-Mann,
                Brueckner (1957); Langreth, Perdew (1977);
                Gunnarsson, Lundqvist (1975, 1976)

RPA :   random phase approximation

Density Functional Theory Key Points

DFT considers the electron density the important function to find rather than the wavefunctions themselves. Hohenberg and Kohn theorems state that this is valid in defining the electronic structure of the ground state.

Kohn-Sham DFT re-invokes single electron wavefunctions, effectively allowing use of the kinetic-energy term from Schrodinger's equation

Kohn-Sham DFT becomes easier to solve than basic wavefunction methods (ie, Hartree-Fock) and plausibly more accurate. The major disadvantage is the need for the "unknown" exchange and correlation functional

Many exchange and correlation functionals exist. The choice of which to use depends on the system of interest, previous testing of functionals on the system, and computational power available.

The first idea towards DFT

➢ DFT started with **the Thomas-Fermi approach** (late 20's and early 30's).

➢ **The basic idea is that the wave function of many-body interacting problem is too difficult to work with. It will be nice if we treat it with a single scalar object such as the charge density**. Effectively, we move from the complexity of

$$\psi(\vec{r}_1,...,\vec{r}_n, \vec{R}_1,...,\vec{R}_N)$$

to a scalar charge density field $\rho(x,y,z)$.

➢ Thomas and Fermi posed the problem as follows: Can we try to solve not for the many body wave function in the Schrödinger equation but rather **solve some other equation where the only unknown is the charge density**.

➢ **The charge density will be treated as a fundamental variable in the solution of the interacting many electron problem**.

Hohenberg-Kohn theorem: key statements

- **The nondegenerate GS wave function is unique functional of GS density**

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2 \ldots, \mathbf{r}_N) = \Psi[n_0(\mathbf{r})]$$

$$O_0 = O[n_0] = \langle \Psi[n_0] | \hat{O} | \Psi[n_0] \rangle$$

- **GS energy is given expectation value of ground state wave function**

$$E_{v,0} = E_v[n_0] = \langle \Psi[n_0] | \hat{H} | \Psi[n_0] \rangle$$

$$E_v[n_0] \leq E_v[n']$$

Capelle, *Brazilian Journal of Physics*, **36, 1318-1343, 2006**