



UNIVERSITY of
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KYA323

Atomic physics

Andy McCulloch





Early atomic physics

Foot Ch. 1



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Learning outcomes

Week 1, lecture 1

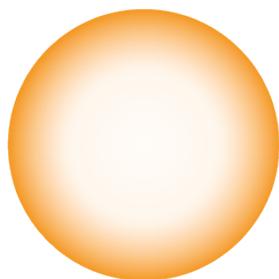
Foot §1.1 – 1.3, 1.5, 1.6

Pre-Schrödinger atomic physics (a review)

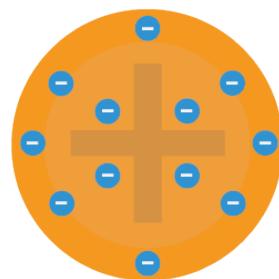
- The hydrogen spectrum
- Bohr's theory
- Moseley's law
- Radiative lifetime

Introduction

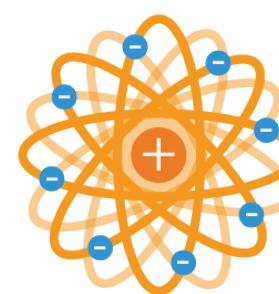
- The development of atomic physics is intertwined with the development of quantum mechanics
- Simple models can help build intuition for atomic structure and transitions
- The interplay between theoretical and experimental discoveries drove the advancement in our understanding



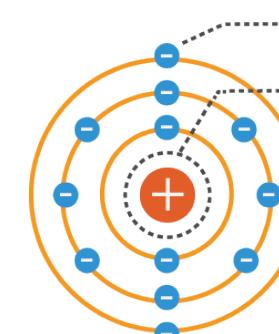
Solid sphere model
(Dalton, 1803)



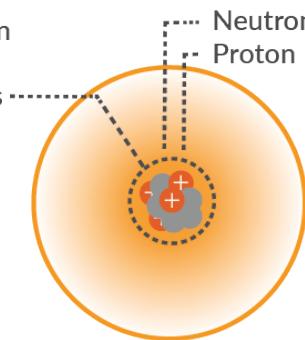
Plum pudding model
(Thomson, 1897)



Nuclear model
(Rutherford, 1911)



Planetary model
(Bohr, 1913)



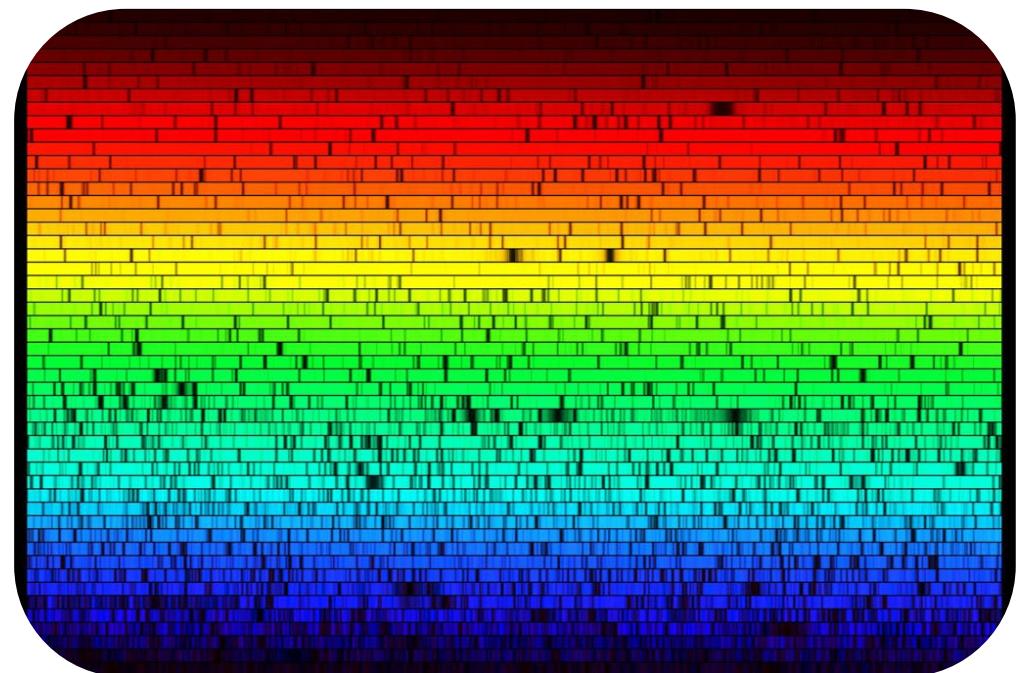
Quantum model
(Schrodinger, 1926)

Atomic spectra

- It was long known that light emitted by an element is characteristic to the element
- Advances in spectroscopy led to the discovery of many elements
 - E.g. Helium from the solar spectrum
- How to explain these absorption/emission lines?



Sodium in a flame



A high-resolution solar spectrum



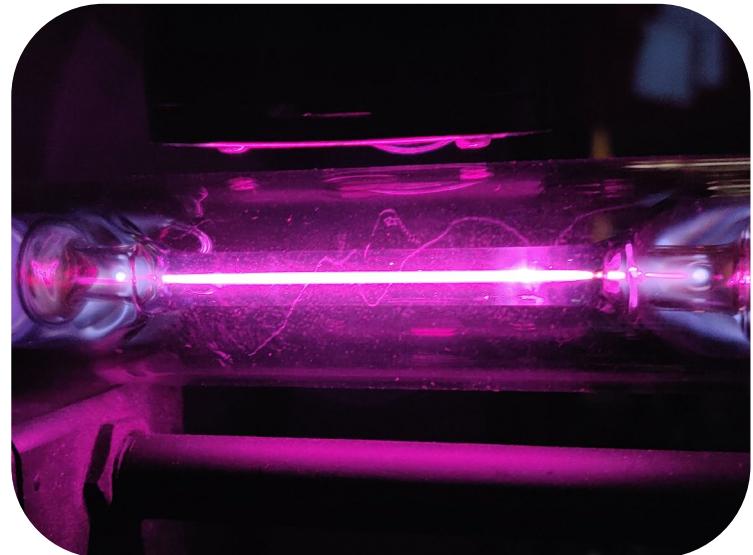
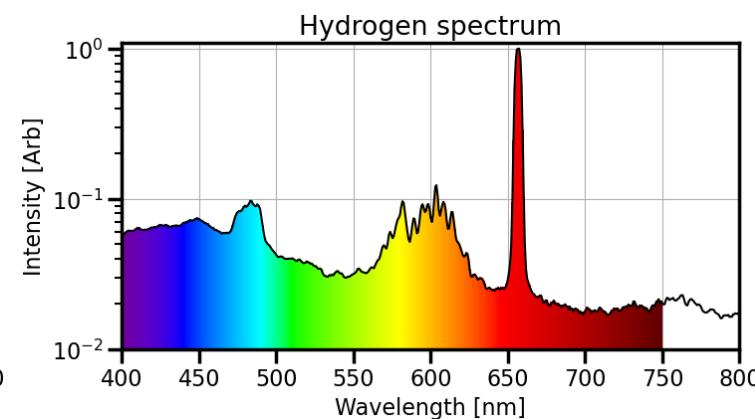
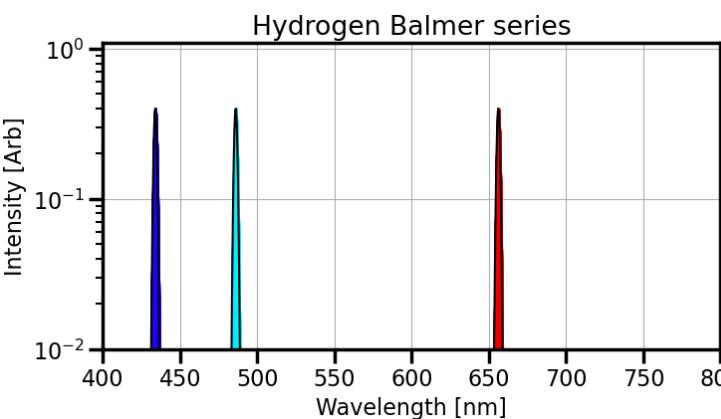
Spectrum of atomic hydrogen

In 1888, Johannes Rydberg found that the Hydrogen spectral lines obey

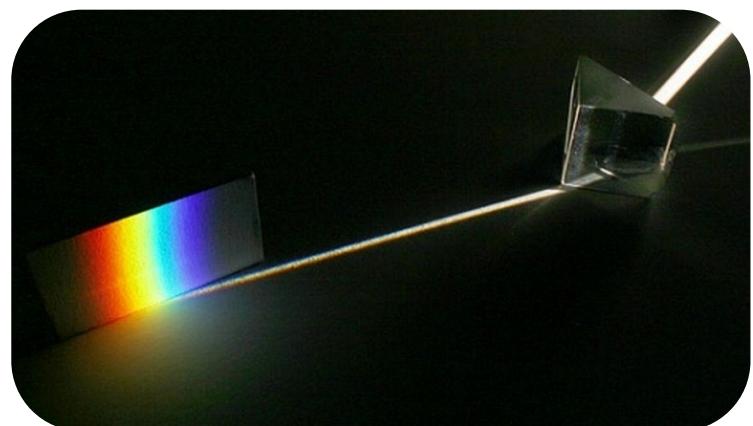
$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{n'^2} \right), n, n' \in \mathbb{N}$$

where R_H is the Rydberg constant

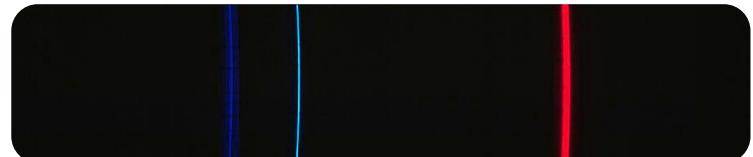
$$R_H \approx 1.09678 \times 10^7 \text{ m}^{-1}$$



A hydrogen discharge lamp



A prism separating white light



The hydrogen emission spectrum

Spectrum of hydrogen-like atoms

In 1913, Bohr proposed his model of the atom and quantisation, arriving at

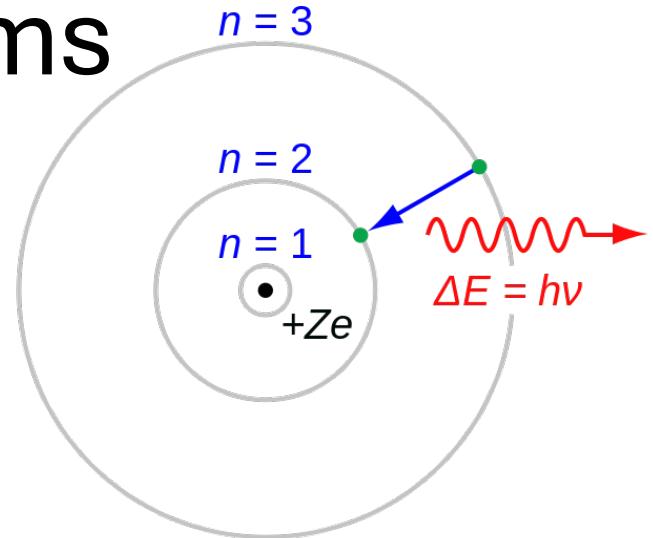
$$\tilde{\nu} = R_\infty \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

where $\tilde{\nu} = 1/\lambda$ is the wavenumber, n is the principal quantum number, and

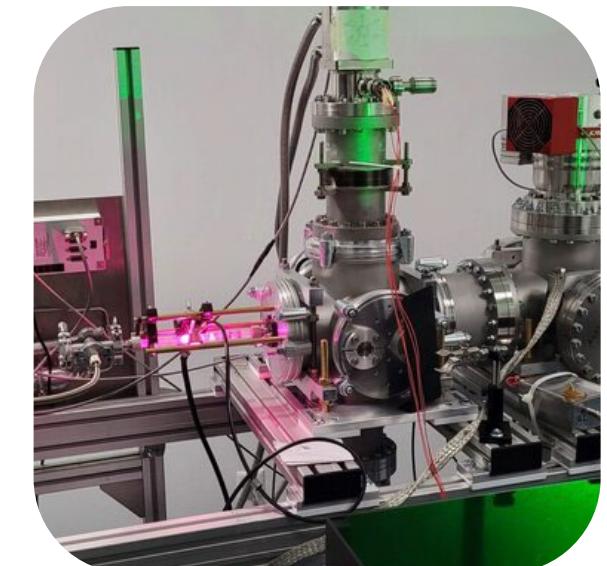
$$hcR_\infty = \frac{\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 m_e}{2\hbar^2}$$

with

$$\underline{R_\infty = 10,973,731.568160(21) \text{ m}^{-1}}$$



The Bohr model of the atom



Precision measurements of hydrogen

Reduced mass

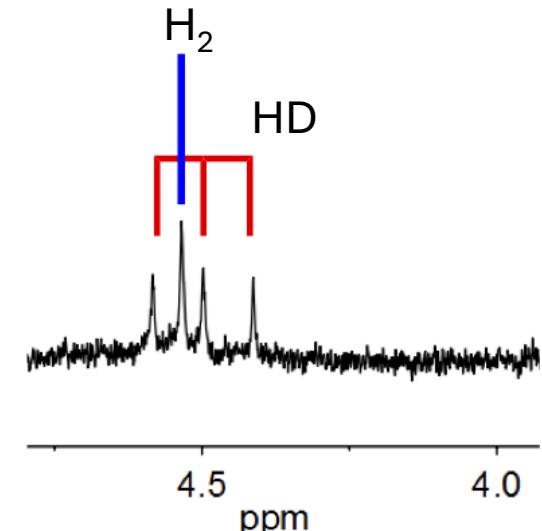
R_∞ is the Rydberg constant calculated for an electron orbiting a fixed nucleus (an infinitely heavy nucleus). In reality, both electron and proton move around the centre of mass.

For a finite nuclear mass m_N , the reduced mass must be used in place of m_e and is defined by

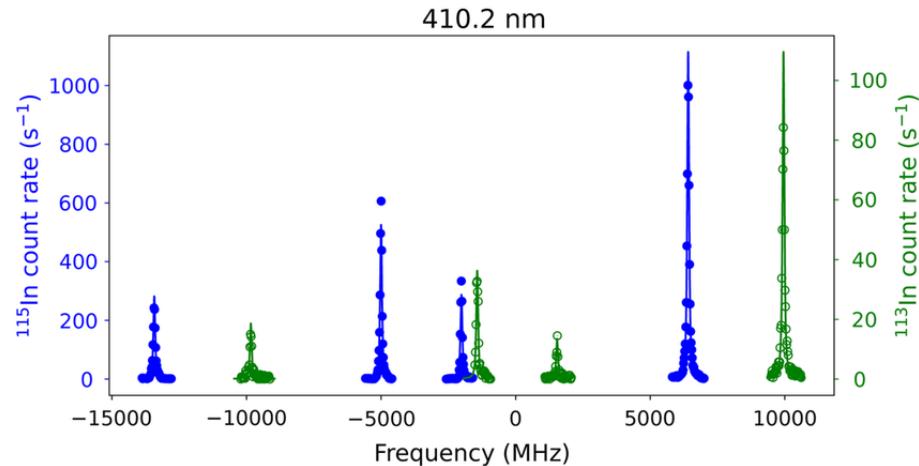
$$\mu = \frac{m_e m_N}{m_e + m_N}$$

and for hydrogen

$$R_H = R_\infty \frac{m_p}{m_e + m_p} \approx R_\infty \left(1 - \frac{m_e}{m_p} \right)$$



NMR spectrum of H_2



Isotope shift for Indium 113 and 115



Moseley's law

Mosely observed that the frequency of X-ray f emitted as a function of atomic number obeyed

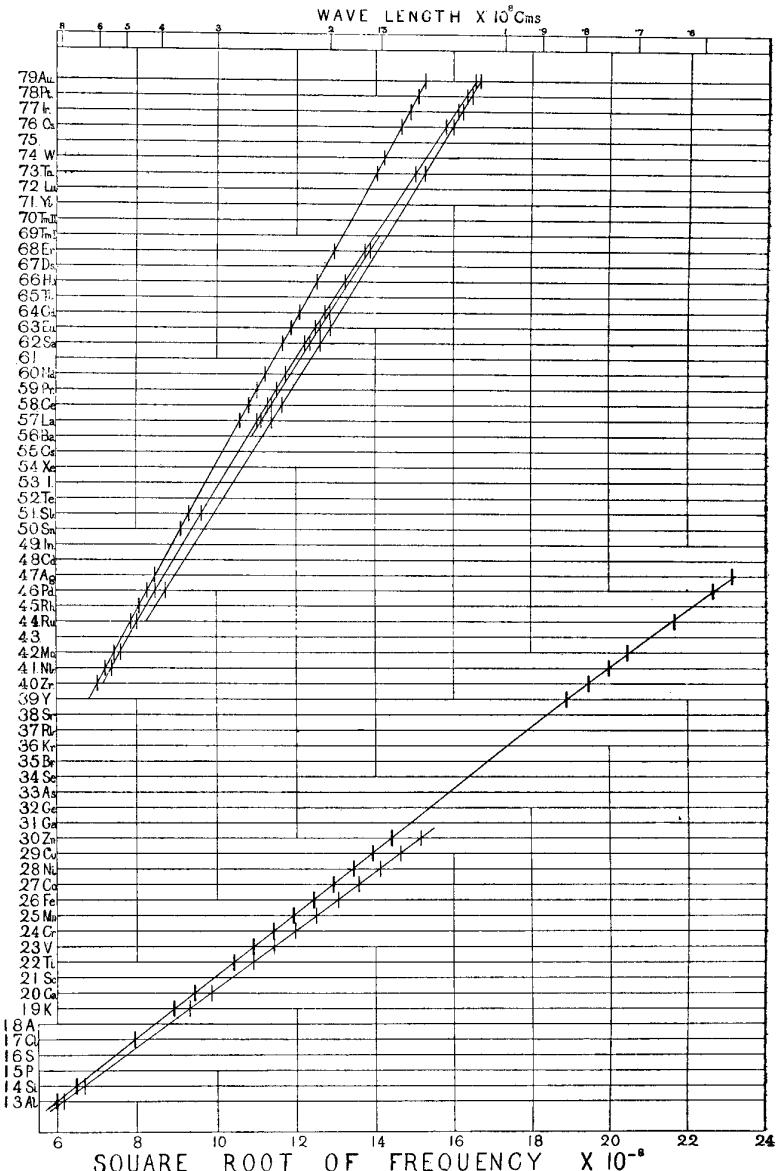
$$\sqrt{f} \propto Z$$

Can obtain consistency with the Bohr model if the electrons sequentially “fill” the predicted shells, but only with a specific of electrons per shell ($N = 2$ for $n = 1$, $N = 8$ for $n = 2$, etc.), and

$$\frac{e^2}{4\pi\epsilon_0} \rightarrow \frac{Ze^2}{4\pi\epsilon_0}$$

$$\frac{1}{\lambda} = R_\infty \left(\frac{(Z - \sigma_n)^2}{n^2} - \frac{(Z - \sigma_{n'})^2}{n'^2} \right)$$

Fig. 3.



The high-frequency spectra of the elements

Radiative decay

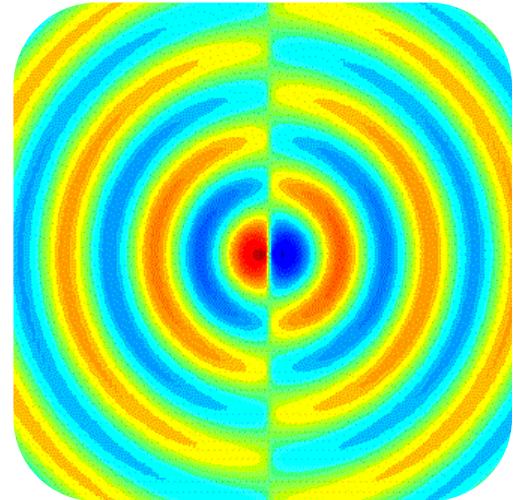
An electric dipole moment $-ex_0$ oscillating at angular frequency ω radiates power:

$$P = \frac{e^2 x_0^2 \omega^4}{12\pi\epsilon_0 c^3}$$

An electron in harmonic motion has a total energy $E = m_e \omega^2 x_0^2 / 2$, which will be dissipated at a rate equal to the power radiated:

$$\frac{dE}{dt} = \frac{e^2 \omega^2}{6\pi\epsilon_0 m_e c^3} E = -\frac{E}{\tau}$$

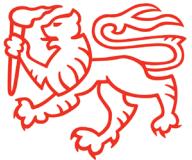
where the classical lifetime $\tau = \frac{e^2 \omega^2}{6\pi\epsilon_0 m_e c^3}$



Radiation emitted from a dipole

Element	λ [nm]	τ_{act} [ns]	τ_c [ns]
Hydrogen	121.57	1.60	0.67
Lithium	670.96	26.87	20.25
Sodium	589.16	15.90	15.61
Rubidium	780.24	26.63	27.38
Caesium	852.35	30.70	32.68

Table of transition lifetimes



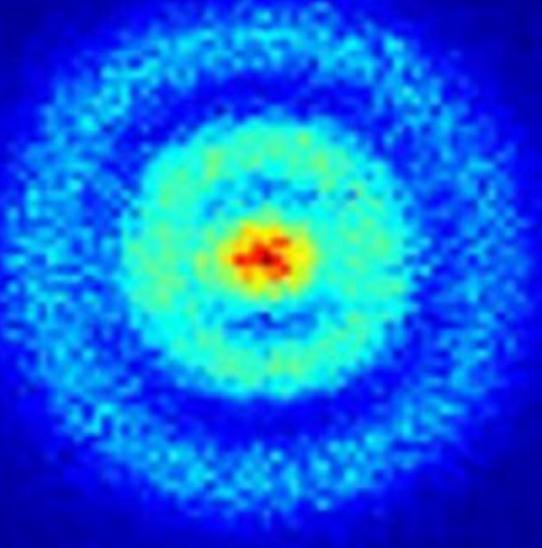
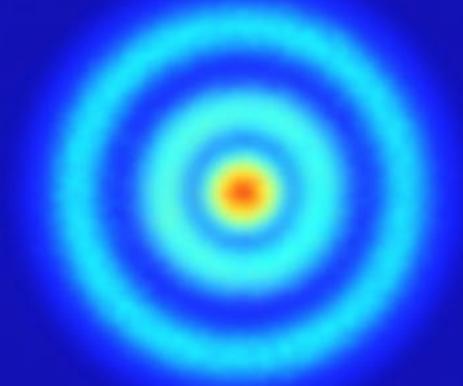
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Summary

Problems

F1.1, F1.2, F1.8, F1.12

- The hydrogen spectrum
 - Atomic transitions described by Rydberg formula
- Bohr's theory
 - Quantisation of atomic energy levels
- Moseley's law
 - Extension of the Bohr model to heavy atoms
- Radiative lifetime
 - Dipole radiation accurately models measured lifetimes



The hydrogen atom

McIntyre Ch. 8 // Foot, Ch. 2

Learning outcomes

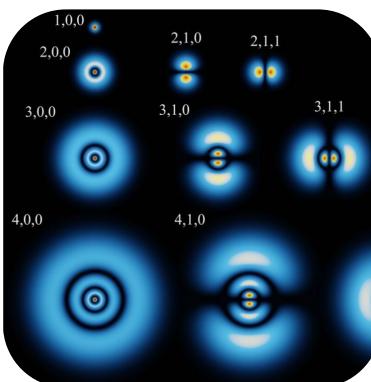
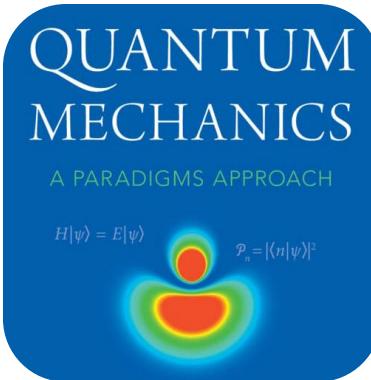
Week 1, lecture 2

McIntyre §8.1 – 8.5 // Foot §2.1: The Hydrogen atom

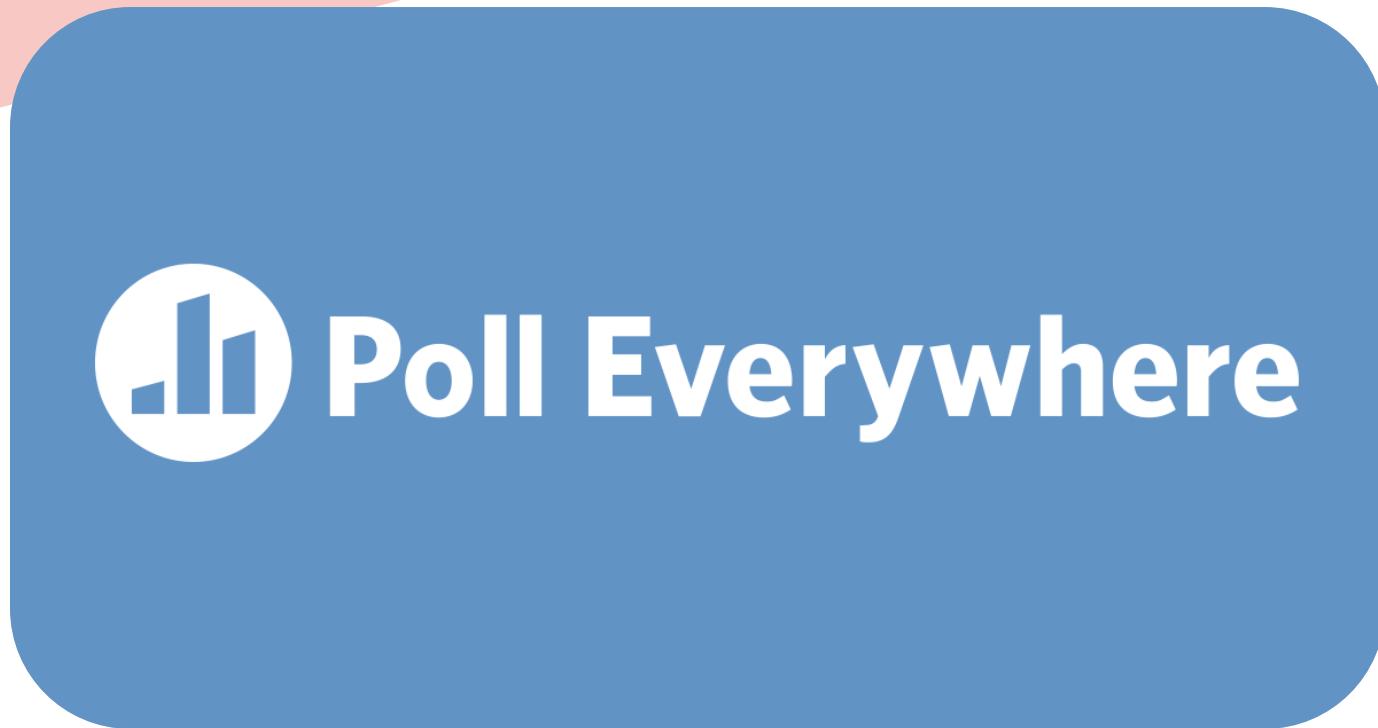
- The Schrödinger equation
 - A brief refresher
- Solving the Schrödinger equation for Hydrogen
 - Atomic units
 - Angular and radial wavefunctions
 - Spectroscopic notation

Why study the Hydrogen atom?

1. Simplest atom that can be described by quantum mechanics
2. Hydrogen has always been the testbed for atomic models
3. Introduces quantum numbers, electron orbitals
 - Critical for understanding more complex atoms, bonds, molecules
4. Most abundant element in the universe
 - Essential to understand astrophysics and cosmology
5. Gateway to advanced quantum



Feel the love



A QR code to *Poll Everywhere*
<https://pollev.com/andym360>



When poll is active respond at PollEv.com/andym360

Barium is used to make which colour firework?

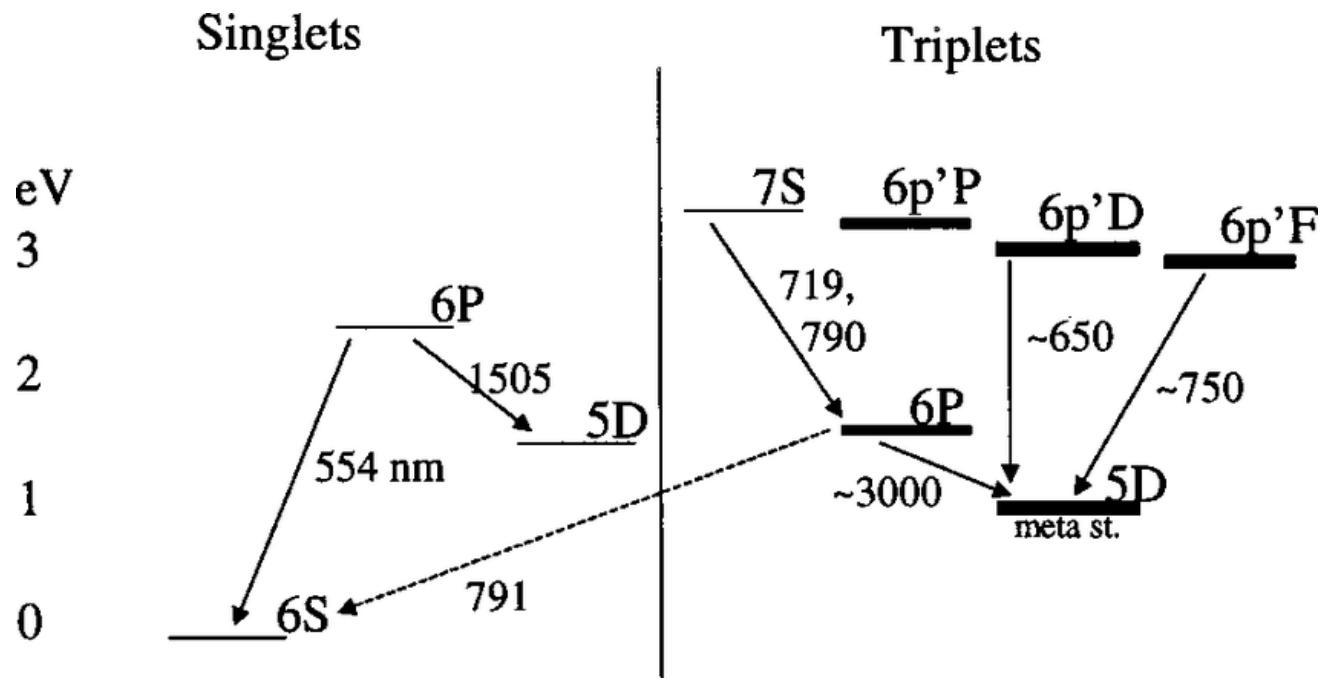
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Barium is used to make which colour firework?



Barium salts are used to make green fireworks



The energy-level structure of neutral barium



When poll is active respond at PollEv.com/andym360



The statement $\hat{H}|\Psi\rangle = E|\Psi\rangle$ is always true

Correct



Incorrect





Schrödinger equation refresher

The (time-dependent) Schrödinger equation is given by

$$i\hbar \frac{d}{dt} |\Psi\rangle = \hat{H}|\Psi\rangle$$

The time-independent Schrödinger equation is

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

where

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



Erwin Schrödinger (46) in 1933

Atoms with one electron

For an electron interacting with the Coulomb field of a nucleus of charge $+Ze$, the Schrödinger equation is

$$\left[\frac{-\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

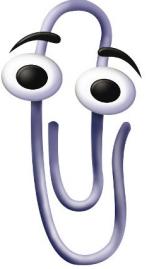
where the reduced mass is

$$\begin{aligned} \mu &= \frac{m_e m_N}{m_e + m_N} \\ &\approx \frac{m_e \cdot 1836m_e}{m_e + 1836m_e} \approx m_e \end{aligned}$$

which is used as the coordinates are selected to be at the centre of mass of the system.

Atomic (Hartree) units

*Convention = convenience



Define a set of units which

$$m_e = \hbar = e = \frac{1}{4\pi\epsilon_0} = 1$$

Then with $\mu \approx m_e$ the Schrödinger equation becomes

$$\left[\frac{1}{2} \nabla^2 - \frac{Z}{r} \right] \psi(\mathbf{r}) = E\psi(\mathbf{r})$$



Douglas Hartree in 1897

It is convention to use these units, or SI units, as situation dictates

Atomic unit	Expression [a.u.]	Value [SI]	Expression [SI]
Length	a_0	52.9 pm	$\frac{4\pi\epsilon_0\hbar^2}{e^2m_e} = \frac{\hbar}{m_e c \alpha}$
Energy	E_h	0.436 aJ 27.2 eV	$m_e \left(\frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 = \frac{\hbar^2}{m_e a_0^2} = m_e c^2 \alpha^2$

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$$

is the *fine structure constant*

Constant	Value
α	$1/137$
R_∞	$E_h/2 = 13.6 \text{ eV}$
c	$1/\alpha = 137 \text{ a.u.}$

Solving the Schrödinger equation

Solve in spherical polar coordinates, where:

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

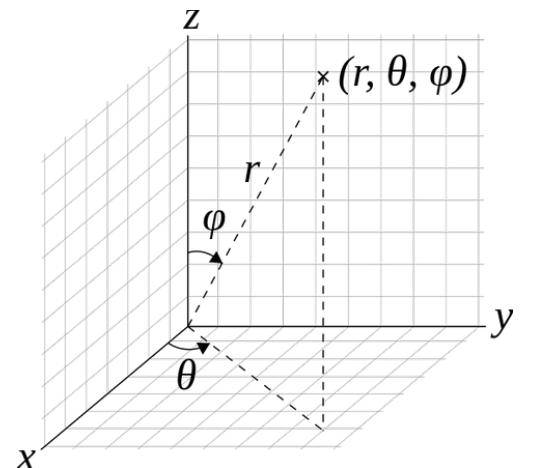
Assume separability

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Then

$$\frac{r^2}{R(r)} \left[\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} + 2 \left(E - \frac{Z}{r} \right) R(r) \right] = \Lambda$$

$$= -\frac{1}{Y(\theta, \phi)} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right]$$



Spherical polar coordinates

Solution to the angular equation

The solutions to the angular component are given by the *spherical harmonic functions*

$$Y(\theta, \phi) = Y_l^m(\theta, \phi)$$

which for a given value of l , there are $2l + 1$ independent solutions, one for each integer m with $-l \leq m \leq l$

$$Y(\theta, \phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\phi} P_l^m(\cos \theta)$$

where P_l^m is the associated *Legendre polynomial* of degree l and order m :

$$P_l^m(x) = (-1)^m 2^l (1-x^2)^{m/2} \sum_{k=m}^l \frac{k!}{(k-m)!} x^{k-m} \binom{l}{k} \binom{l+k-1}{l}$$



The only known image of
Adrien-Marie Legendre

Solving to the radial equation

The separation constant $\Lambda = l(l + 1)$ which gives

$$\frac{d^2R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} - \frac{l(l + 1)R(r)}{r^2} + 2\left(E - \frac{Z}{r}\right)R(r) = 0$$

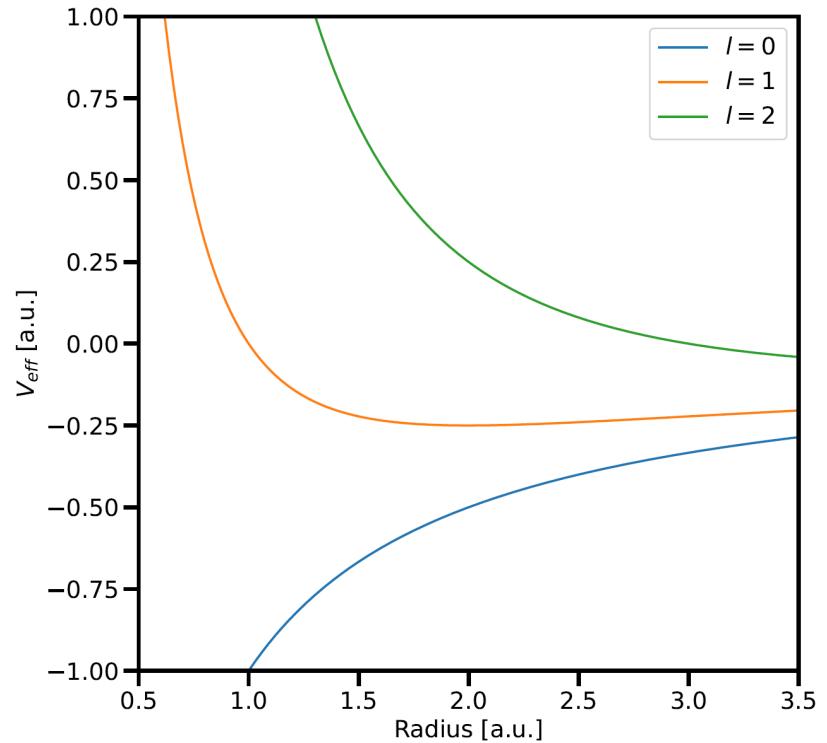
Defining $R(r) = u(r)/r$

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + V_{eff}(r) \right] u(r) = Eu(r)$$

where

$$V_{eff}(r) = -\frac{Z}{r} + \frac{l(l + 1)}{r^2}$$

Note that only $l = 0$ has probability amplitude near the nucleus



Effective potential for different values of l

Solution to the radial equation

The solution to the radial component of the wavefunction is given by

$$R_{nl}(r) = \left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{(2n)[(n+l)!]^3} \right]^{\frac{1}{2}} \left(\frac{2Zr}{na_0} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2Zr}{na_0} \right) \exp \left(-\frac{Zr}{na_0} \right)$$

where $L_n^{(\alpha)}(x)$ is the *generalised Laguerre polynomial* of degree n and order α

$$\begin{aligned} L_n^{(\alpha)}(x) &= \sum_{m=0}^n (-1)^m \binom{n+\alpha}{n-m} \frac{x^m}{m!} \\ &= \sum_{m=0}^n (-1)^m \frac{(n+\alpha)!}{(\alpha+m)!(n-m)!m!} x^m \end{aligned}$$

The *Laguerre polynomials* $L_n(x)$ can be generated via

$$L_n(x) = e^x \frac{d^n}{dx^n} (x^n e^{-x})$$

from which the $L_n^{(\alpha)}(x)$ can be generated

$$L_n^{(\alpha)}(x) = \frac{d^\alpha}{dx^\alpha} L_n(x)$$



Edmond Laguerre

Hydrogen wave function

The wavefunction of the hydrogen atom is then given by

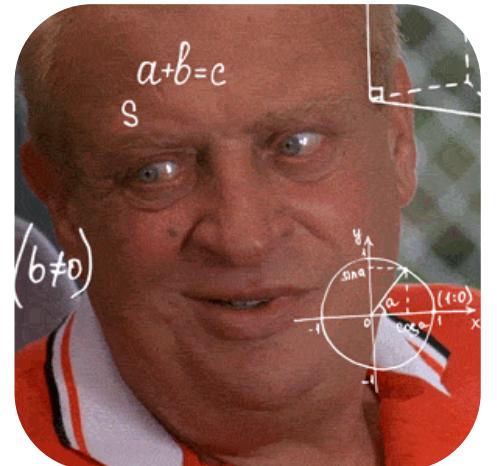
$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi)$$

and satisfies

$$\hat{H}\psi_{nlm}(r, \theta, \phi) = -\frac{\text{Ry}}{n^2} \psi_{nlm}(r, \theta, \phi) = -\frac{13.6 \text{ eV}}{n^2} \psi_{nlm}(r, \theta, \phi)$$

$$\hat{L}^2\psi_{nlm}(r, \theta, \phi) = l(l + 1)\hbar^2\psi_{nlm}(r, \theta, \phi)$$

$$\hat{L}_z\psi_{nlm}(r, \theta, \phi) = m\hbar\psi_{nlm}(r, \theta, \phi)$$



Lots of maths

Interactive visualiser (web based)

Explicit energy eigenstate wavefunctions

$$\psi_{100}(r, \theta, \varphi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

$$\psi_{200}(r, \theta, \varphi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{2a_0} \right)^{3/2} \left[1 - \frac{Zr}{2a_0} \right] e^{-Zr/2a_0}$$

$$\psi_{210}(r, \theta, \varphi) = \frac{1}{2\sqrt{\pi}} \left(\frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos \theta$$

$$\psi_{21\pm 1}(r, \theta, \varphi) = \mp \frac{1}{2\sqrt{2\pi}} \left(\frac{Z}{2a_0} \right)^{\frac{3}{2}} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin \theta e^{\pm i\varphi}$$

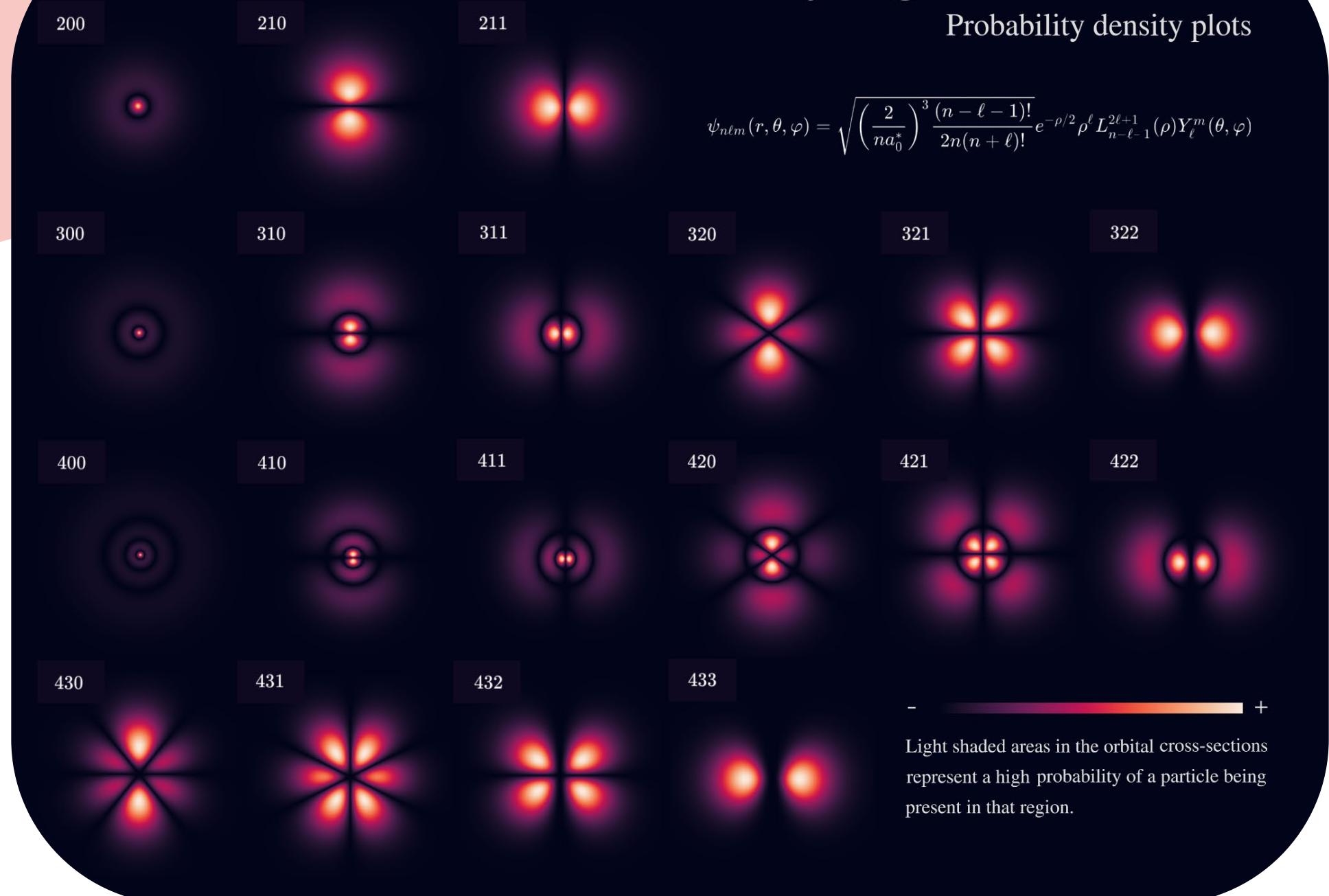
$$\psi_{300}(r, \theta, \varphi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{3a_0} \right)^{3/2} \left[1 - \frac{2Zr}{3a_0} + \frac{2}{27} \left(\frac{Zr}{a_0} \right)^2 \right] e^{-Zr/3a_0}$$

$$\psi_{310}(r, \theta, \varphi) = \frac{2\sqrt{2}}{3\sqrt{3}\pi} \left(\frac{Z}{3a_0} \right)^{\frac{3}{2}} \frac{Zr}{a_0} \left(1 - \frac{Zr}{6a_0} \right) e^{-Zr/3a_0} \cos \theta$$

⋮

Hydrogen Wavefunction

Probability density plots



State labels

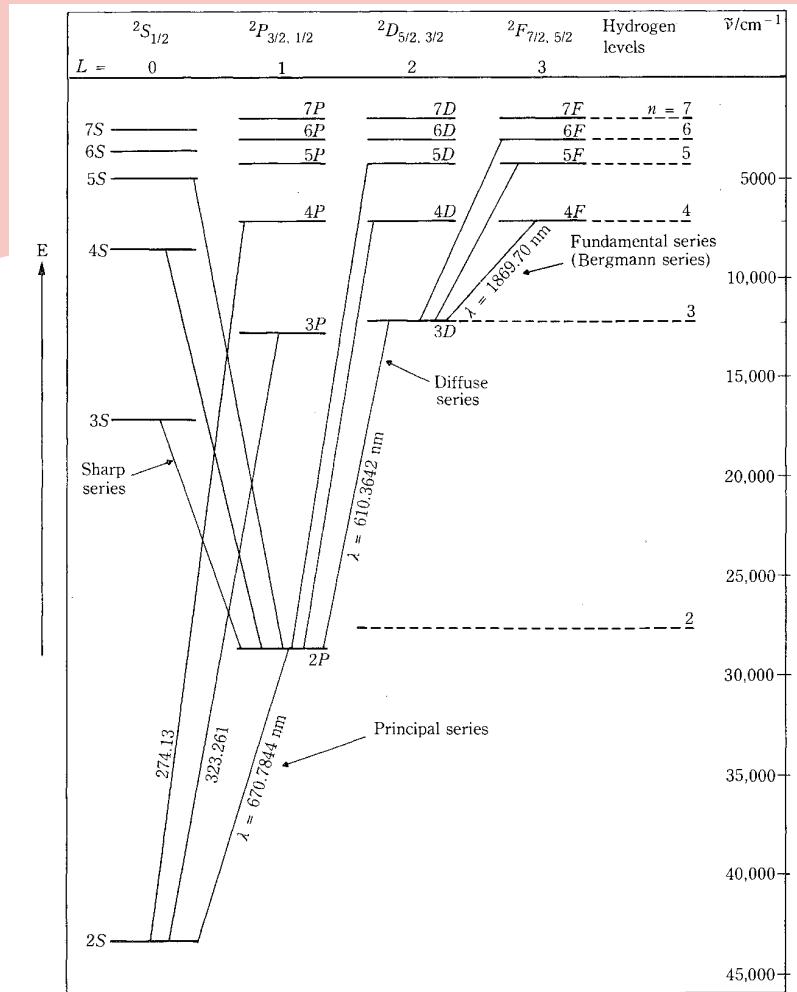


Figure 24.8 Energy-level diagram for the lithium atom. Dashed lines are the corresponding levels for the hydrogen atom. Numbers on the transition lines are the wavelengths in nanometres.

Energy-level diagram for lithium

Orbital number (l)	Label	Original name
0	<i>s</i>	Sharp
1	<i>p</i>	Principal
2	<i>d</i>	Diffuse
3	<i>f</i>	Fundamental
4	<i>g</i>	
⋮	⋮	(alphabetical)

Letter assignments for different values of l

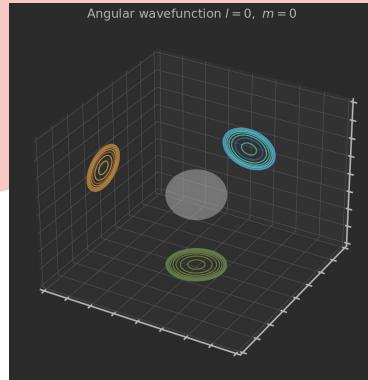
Shell number (n)	Orbital number (l)	Spectroscopic label
1	0	1s
2	0	2s
2	1	2p
3	0	3s
3	1	3p
3	2	3d

Spectroscopic assignments for different values of n and l

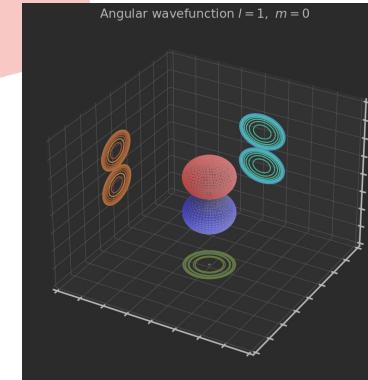
Magnetic quantum number (m)

0

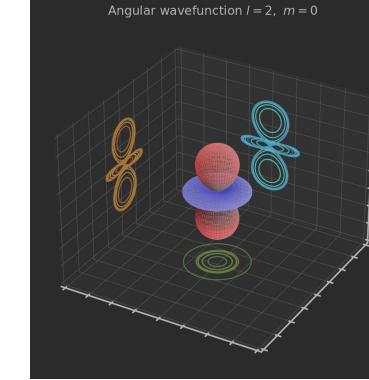
$\ell = 0$



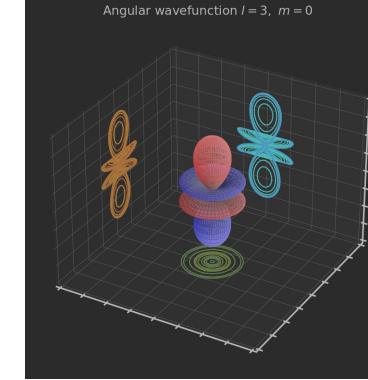
$\ell = 1$



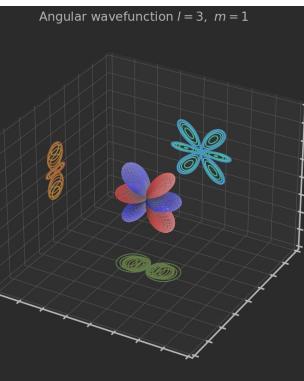
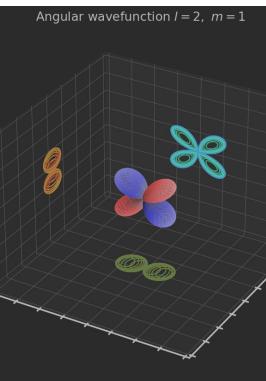
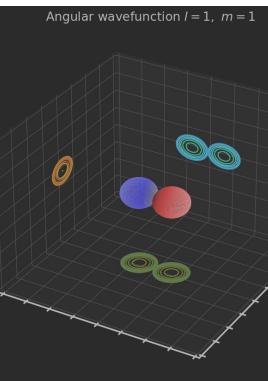
$\ell = 2$



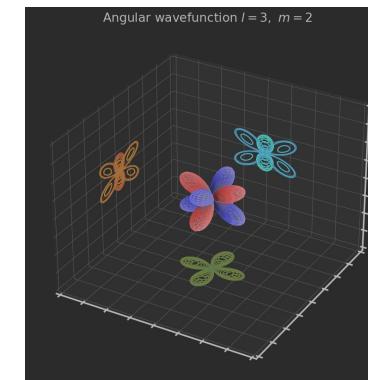
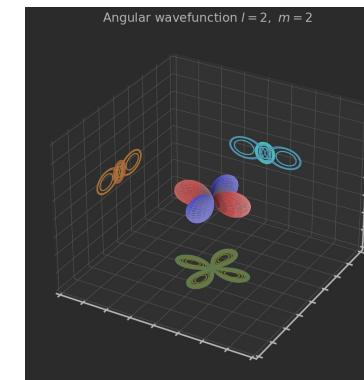
$\ell = 3$



1



2

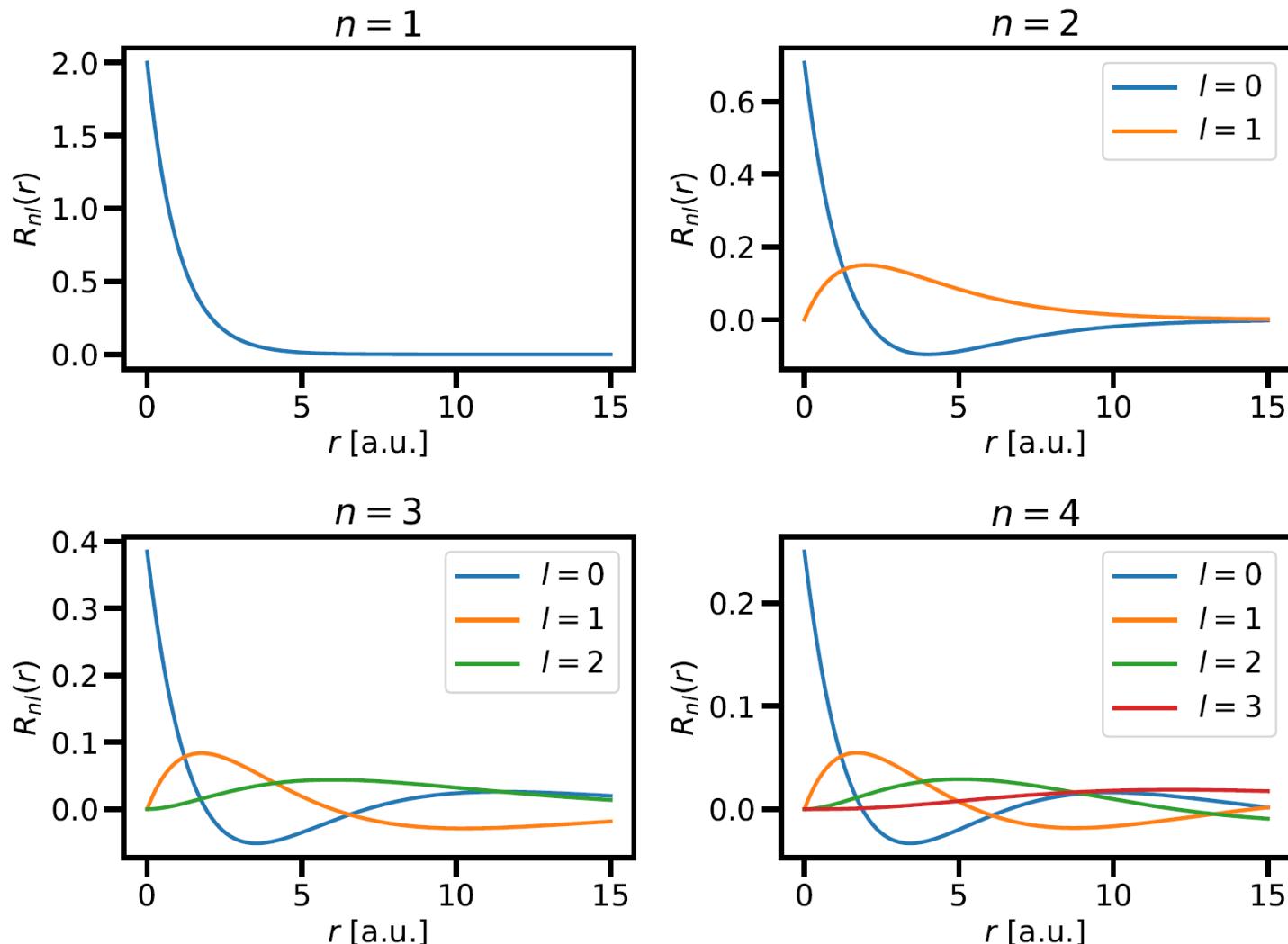


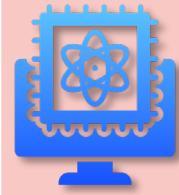
The radial wavefunction

- Higher energy, more nodes ($n - l - 1$)
- All radial functions have r^l dependence

Note the large value of the wavefunction at $r = 0$. How do we understand this?

Radial component of the Hydrogen wavefunction



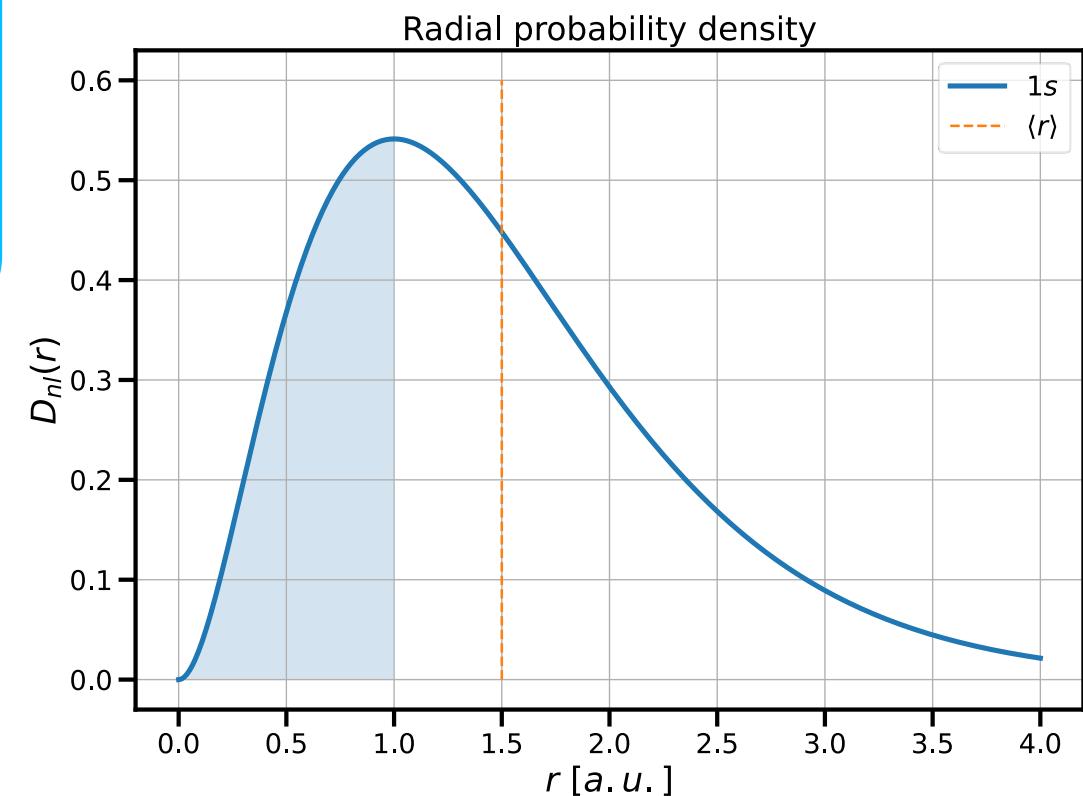


Let's do some computation

Find the probability that the electron in the ground state of hydrogen is measured to be within one Bohr radius of the nucleus, and find the expectation value of the radial position r .

$$\mathcal{P}_{r < a_0} = 0.323$$

$$\langle r \rangle = \frac{3a_0}{2Z}$$



Radial probability density

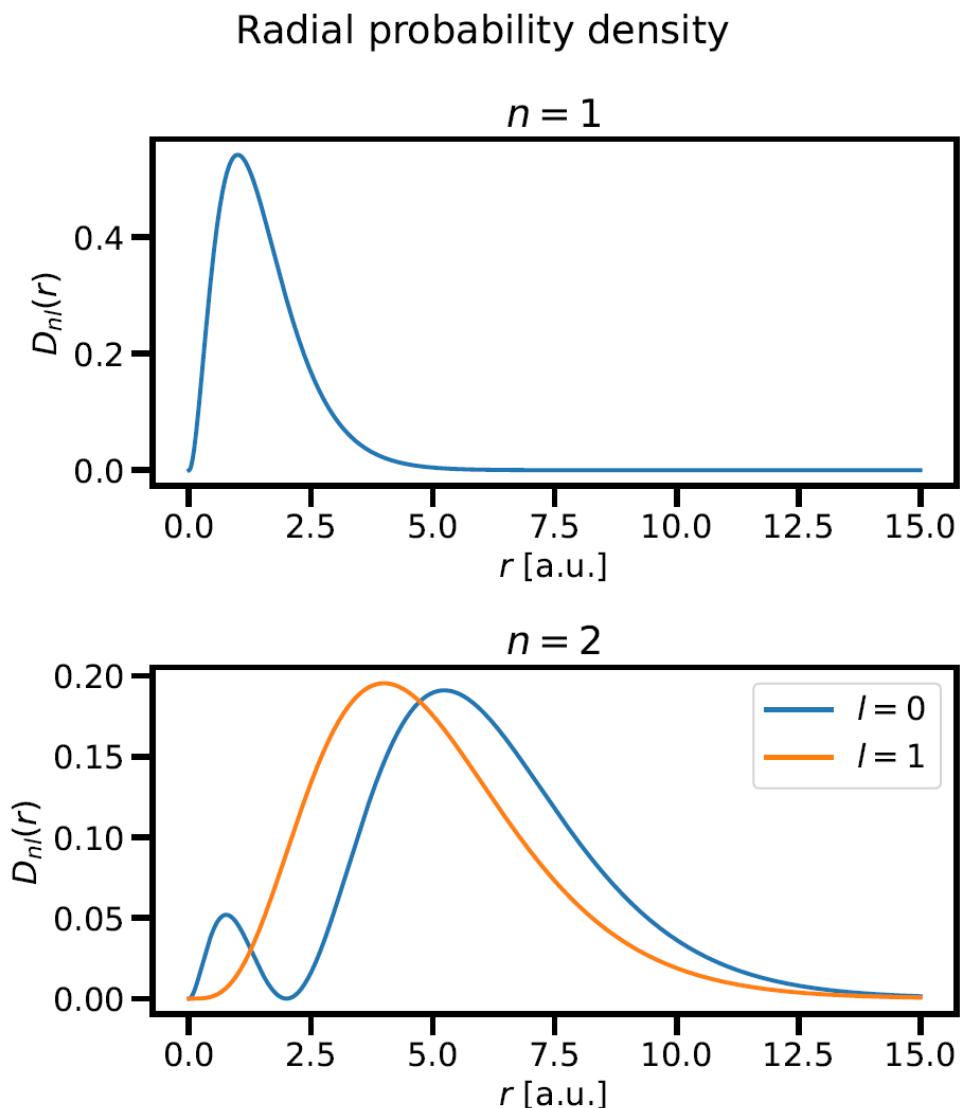
The electron density is given by

$$|R_{nl}(r)|^2$$

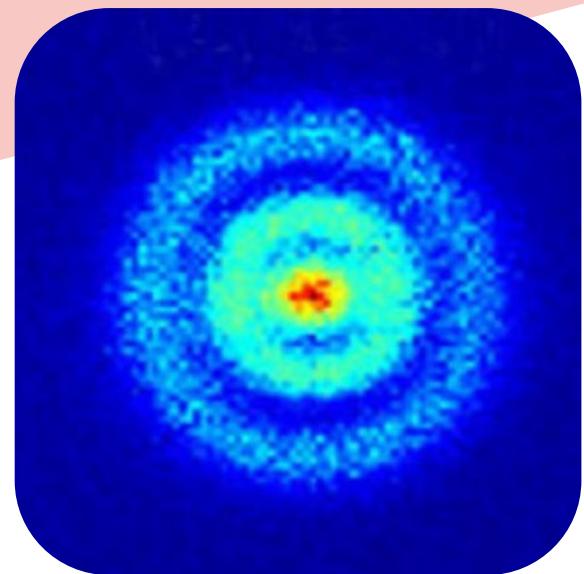
The radial probability density is given by

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

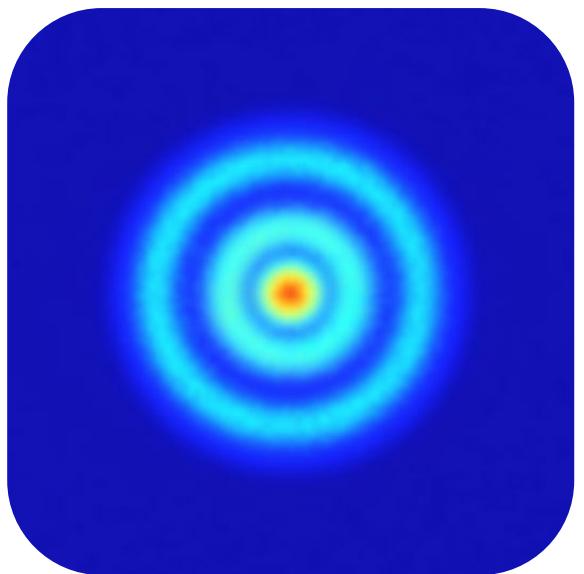
which is the probability of finding the electron between radius r and dr .



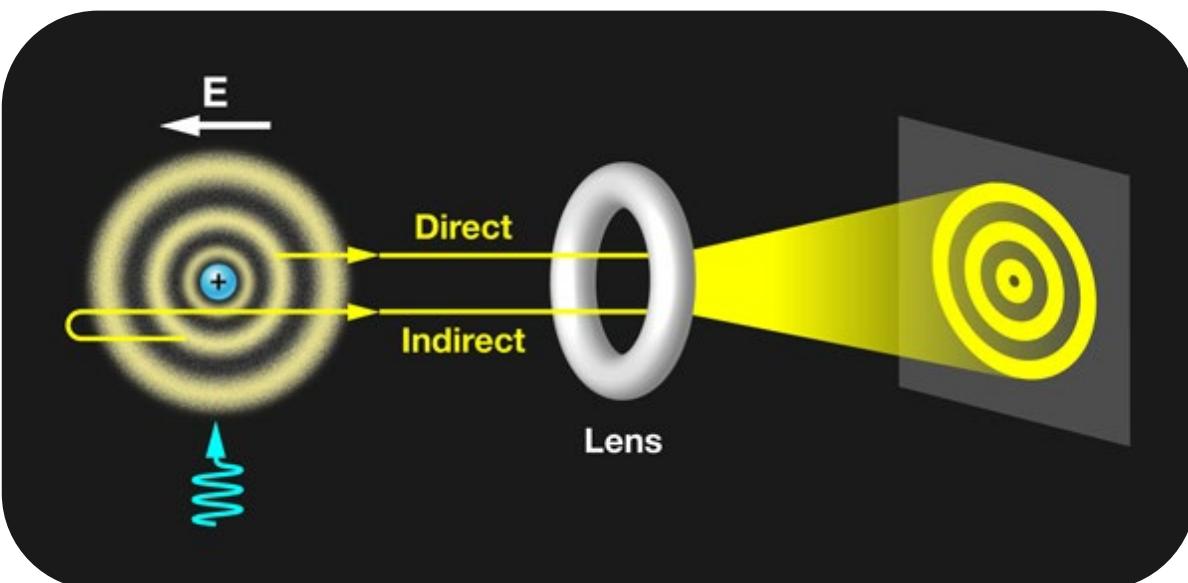
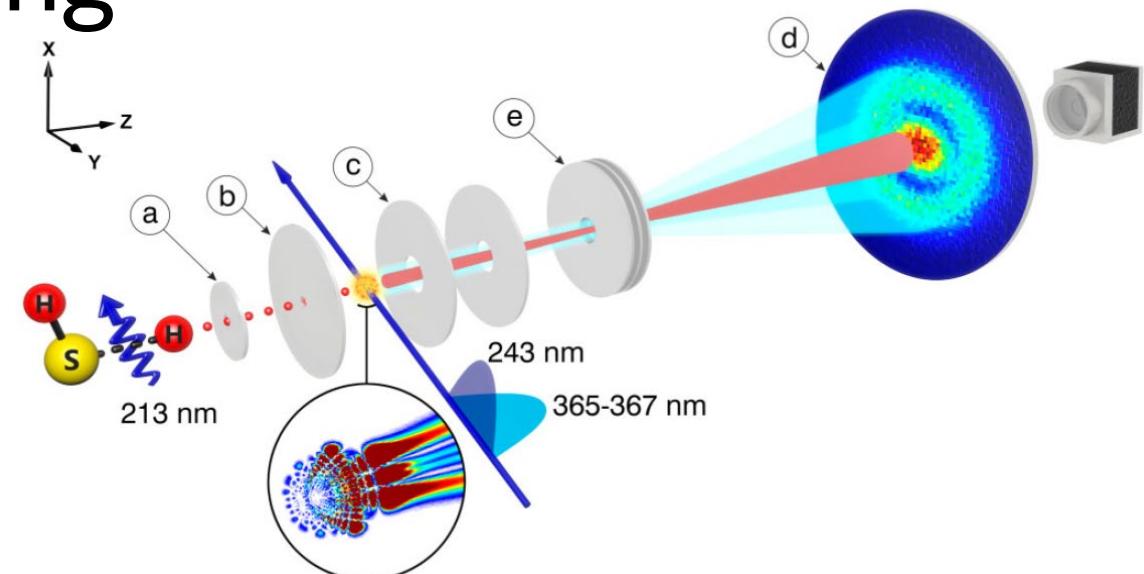
Let's do some measuring



*A measured
wavefunction of
Hydrogen*



*Simulated
wavefunction of
Hydrogen*



Hydrogen atoms under magnification



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Summary

Problems

M8.5, M8.6, M8.12, F2.3

- The Schrödinger equation
 - Simple to write, hard to solve!
- Solving the Schrödinger equation for Hydrogen
 - Atomic units are convenient for atomic calculations
 - We can write a closed form for the Hydrogen wavefunction
 - Spectroscopic notation is useful for labelling states
 - Additional calculations are required to compute measurable quantities



Crunch time

Problem M8.5: By direct application of the differential operators, verify that the state $|321\rangle = \psi_{321}(r, \theta, \phi)$ is an eigenstate of H , \mathbf{L}^2 , and L_z and determine the corresponding eigenvalues

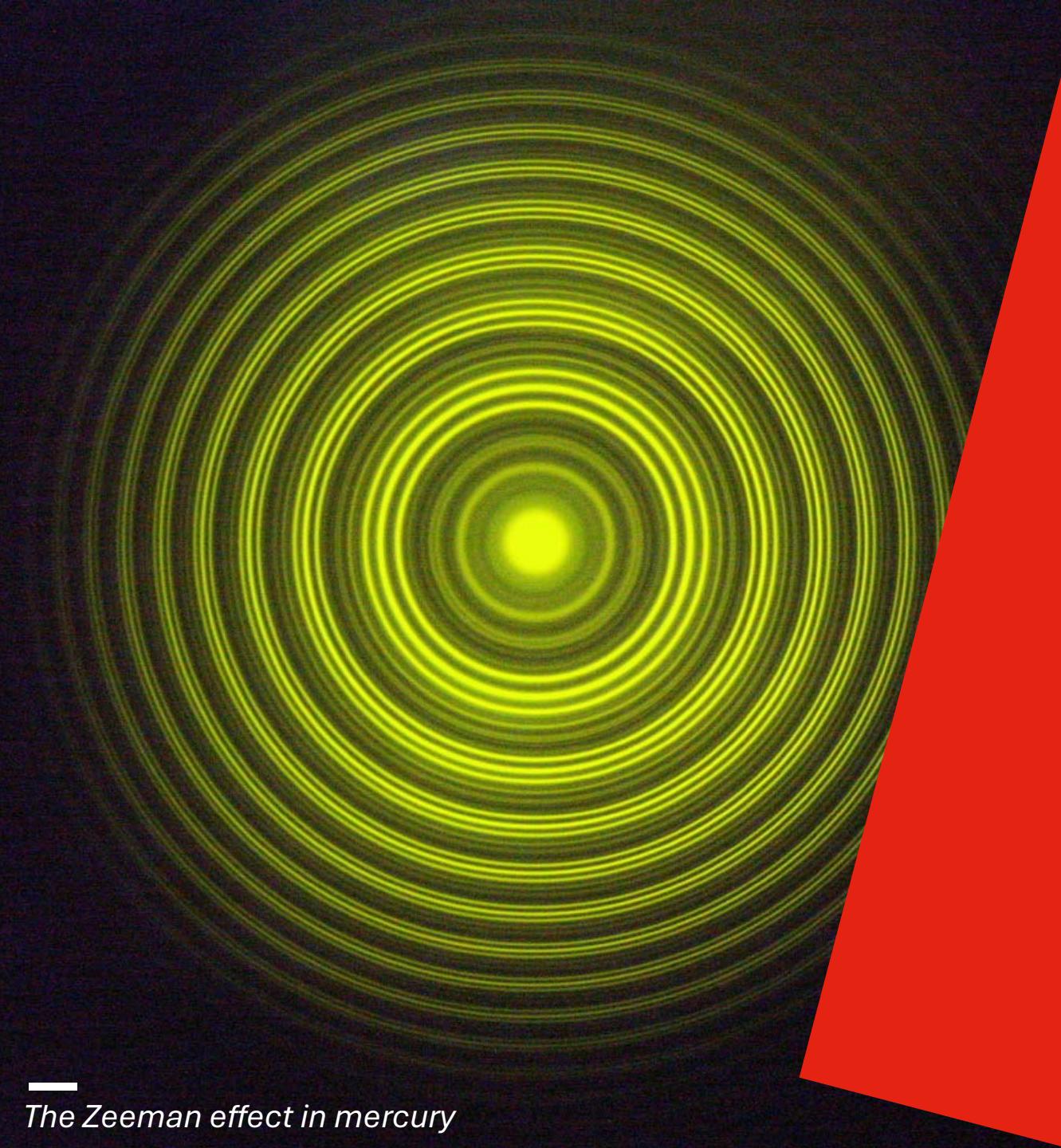
$$\psi_{310}(r, \theta, \phi) = \frac{2\sqrt{2}}{3\sqrt{3\pi}} \left(\frac{Z}{3a_0}\right)^{\frac{3}{2}} \frac{Zr}{a_0} \left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0} \cos \theta$$

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\mathbf{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

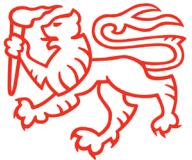
$$\begin{aligned} H &= -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{1}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{1}{\partial \phi^2} \frac{\partial^2}{\partial \phi^2} \right] + V(r) \\ &= -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\mathbf{L}^2}{r^2 \hbar^2} \right] - \frac{Ze^2}{4\pi \epsilon_0 r} \end{aligned}$$

$$L_z|321\rangle = \hbar|321\rangle, \quad \mathbf{L}^2|321\rangle = 6\hbar^2|321\rangle, \quad H|321\rangle = -\frac{Ry}{9}Z^2|321\rangle$$



Calculation methods for real systems

McIntyre Ch. 10



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Learning outcomes

Week 1, lecture 3

McIntyre §10.3, 10.4, 10.6, elsewhere
throughout the text

Calculation methods for real systems

- Perturbation theory
 - A refresher
- The variational method
 - An introduction
 - Examples

Poll position



Poll Everywhere



A QR code to Poll Everywhere
<https://pollev.com/andym360>

When poll is active respond at PollEv.com/andym360



To what extent do you agree with the statement:

I know perturbation theory, and am confident to apply it to a physical system

Agree

0%

Neither agree nor disagree

80%

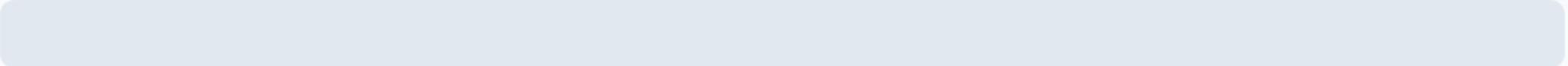
Disagree

20%

Calculate the first-order energy corrections for all levels of an infinite square well potential with a perturbation

$$H' = V_0 \sin(\pi x/L)$$

Let me at it



0%

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Give me some time, then maybe



60%

A horizontal progress bar consisting of a blue rectangular bar with a grey rounded end on the right side.

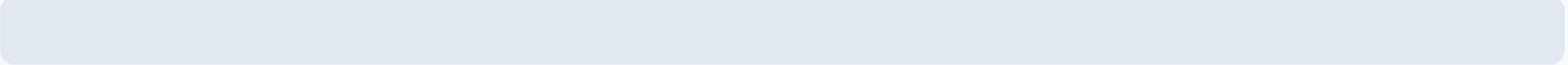
I'd need a nudge, but should be right



40%

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Who is Vosin? Why are they trapped in a well?



0%

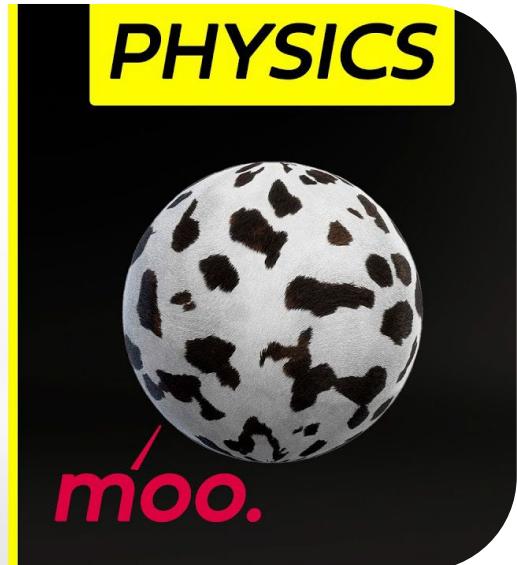
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The real world

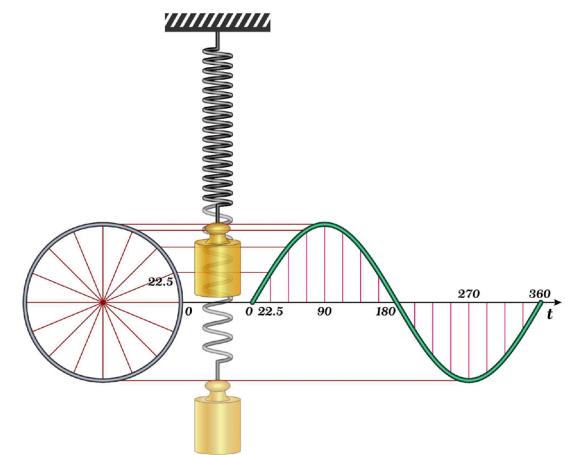
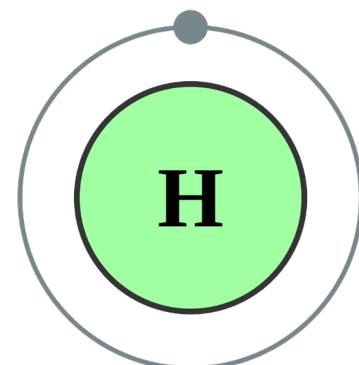
- The Schrödinger equation is hard to solve, so we study simple systems
- Reality is usually more complicated:
 - External fields
 - Non-ideal conditions
 - Interactions
 - Complex systems
- How do we solve the Schrödinger equation for real systems?



REALITY



PHYSICS



Stationary perturbation theory

Begin with exactly solvable part of the problem, the *zeroth-order* problem:

$$H_0|n^{(0)}\rangle = E_n|n^{(0)}\rangle$$

Suppose the system is perturbed by the addition of a new term in the Hamiltonian, H' , yielding

$$(H_0 + H')|n\rangle = E_n|n\rangle$$

Introduce dimensionless quantity λ to quantify strength of perturbation

$$(H_0 + \lambda H')|n\rangle = E_n|n\rangle$$

Perturbation theory: assume we can write new eigenvalues and eigenstates as power series expansions

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \dots$$

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \lambda^3 |n^{(3)}\rangle + \dots$$

Perturbing results

Collect terms of order λ^n :

Order	Terms
$\mathcal{O}(\lambda^0)$	$(H_0 - E_n^{(0)}) n^{(0)}\rangle = 0$
$\mathcal{O}(\lambda^1)$	$(H_0 - E_n^{(0)}) n^{(1)}\rangle = (E_n^{(1)} - H') n^{(0)}\rangle$
$\mathcal{O}(\lambda^2)$	$(H_0 - E_n^{(0)}) n^{(2)}\rangle = (E_n^{(1)} - H') n^{(1)}\rangle + E_n^{(2)} n^{(0)}\rangle$

Take the inner product with $\langle n^{(0)}|$:

$$E_n^{(1)} = H'_{nn} = \langle n^{(0)} | H' | n^{(0)} \rangle$$

$$|n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle m^{(0)} | H' | n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} |m^{(0)}\rangle = \sum_{m \neq n} \frac{H'_{mn}}{(E_n^{(0)} - E_m^{(0)})} |m^{(0)}\rangle$$

Highly perturbing

The first-order wavefunction determines the second-order energy:

$$\begin{aligned} E_n^{(2)} &= \langle n^{(0)} | H' | n^{(1)} \rangle \\ &= \sum_{m \neq n} \frac{\langle m^{(0)} | H' | n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \langle n^{(0)} | H' | m^{(0)} \rangle \\ &= \sum_{m \neq n} \frac{|\langle m^{(0)} | H' | n^{(0)} \rangle|^2}{(E_n^{(0)} - E_m^{(0)})} \end{aligned}$$

Similarly, the third-order energy depends on the second-order wavefunction

A refresher: the harmonic oscillator

The Hamiltonian for a harmonic system is

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$$

The wavefunctions for the system are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2}$$

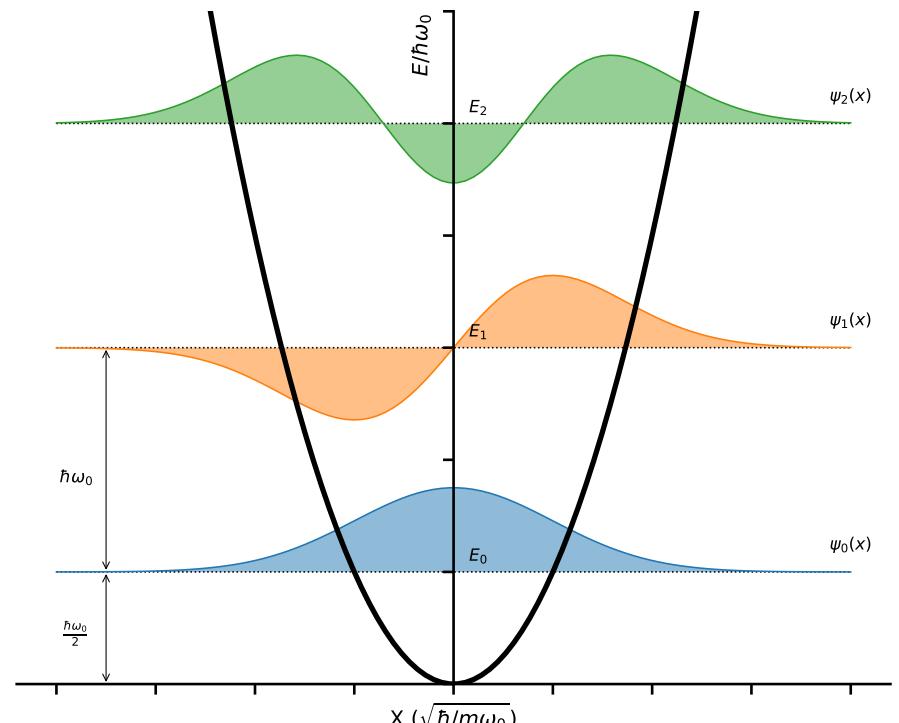
with $\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x$, and $H_n(x)$ the *Hermite polynomial* of order n .

The associated energies are

$$E_n = \hbar\omega(n + 1/2) \text{ for } n \in 0, 1, 2, \dots$$



Charles Hermite

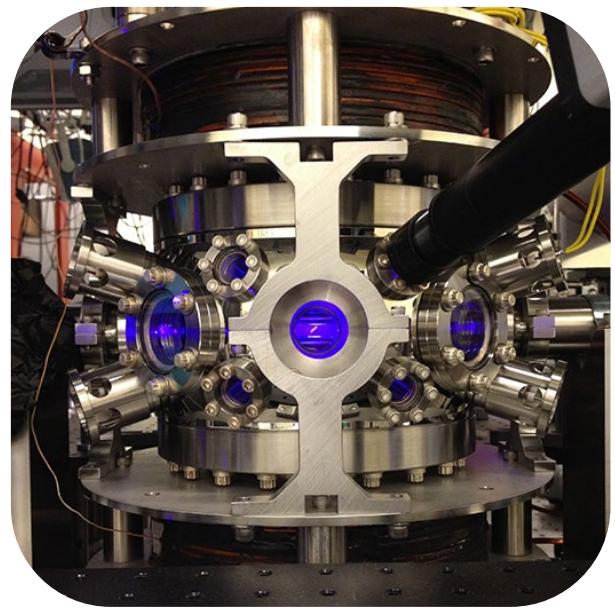


Wavefunctions of the harmonic oscillator



Real-time bonus: treats!?

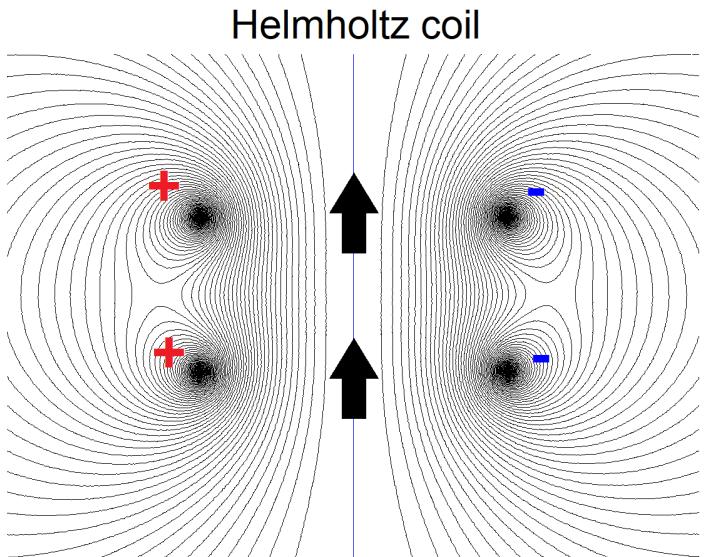
What is an example of a real-world
(quantum) harmonic oscillator system?



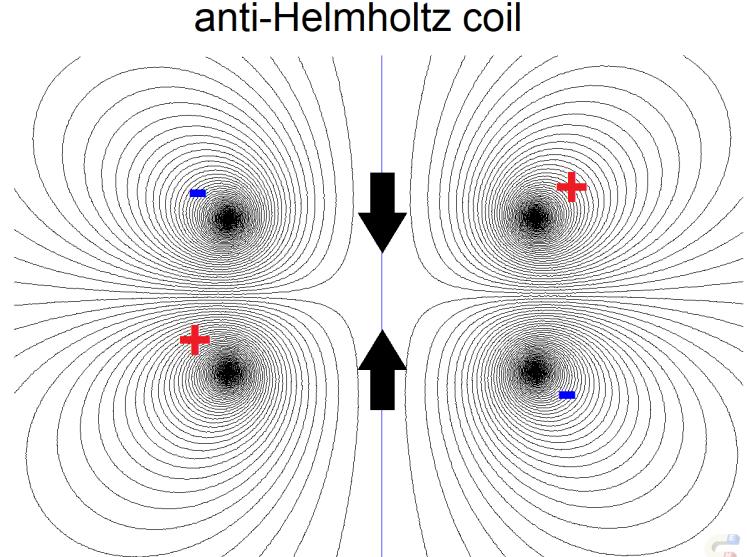
A magnetic (and optical) trap for Ba and Ca



Coils in a Helmholtz configuration

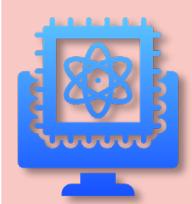


Helmholtz coil



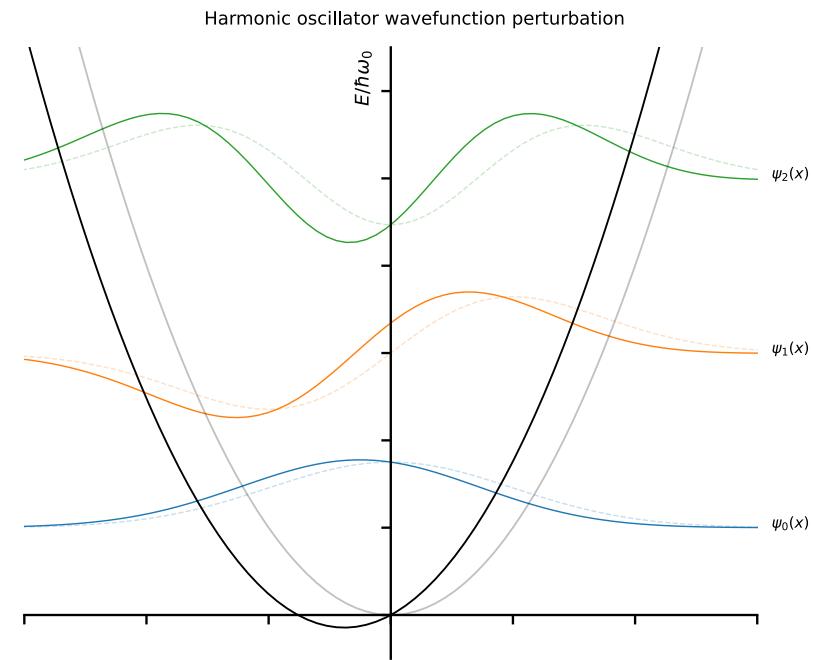
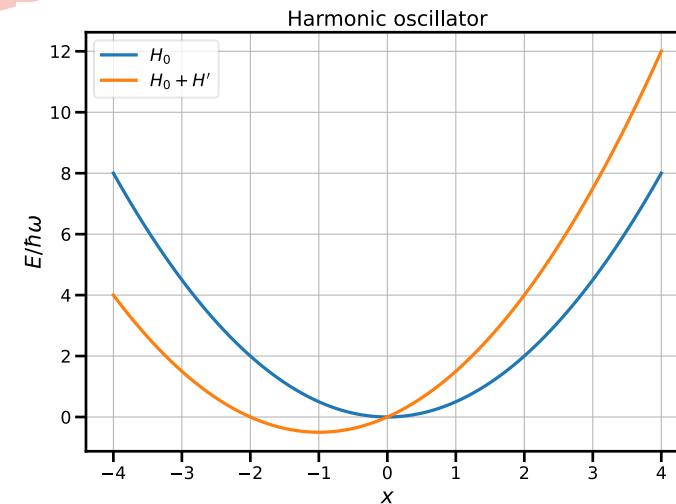
anti-Helmholtz coil

Magnetic field produced using (anti)Helmholtz coils



The perturbed harmonic oscillator

Find E_n and $\psi_n^{(1)}$ for a harmonic oscillator perturbed by a constant electric field $H' = E_0 e \hat{x}$



$$E_n = \hbar\omega \left(n + \frac{1}{2}\right) - \frac{E_0^2 e^2}{2m\omega^2}$$
$$\psi_n^{(1)} = \left(\frac{E_0^2 e^2}{2m\hbar\omega^3}\right)^{\frac{1}{2}} \left(n^{1/2} \psi_{n-1}^{(0)} - (n+1)^{1/2} \psi_{n+1}^{(0)}\right)$$

The variational method: why?

- Perturbation theory is easy to use and provides good estimates of the energy of states
- BUT: perturbed wavefunctions are usually poor and often do not converge
- The variational method is a technique which provides useful estimates for large perturbations
- The method estimates the minimum energy of a state

The variational method: how?

Recipe:

- Make a guess at the wavefunction
- Calculate the variation in energy with respect to some free parameter(s)
- Find the minimum in the energy with respect to the free parameters

Expand an *arbitrary* $|\psi\rangle$ in terms of the eigenvectors of the Hamiltonian

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle \text{ where } H|\phi_n\rangle = E_n |\phi_n\rangle$$

The expectation value of H for state $|\psi\rangle$:

$$\langle H \rangle = \langle \psi | H | \psi \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2$$

where E_0 is the lowest possible energy eigenvalue. For a normalised $|\psi\rangle$:

$$\sum_n |c_n|^2 = 1$$

thus

$$E_0 \leq \langle \psi | H | \psi \rangle$$

or more generally

$$E_0 \leq \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$



Considerations

- Choosing an appropriate trial wavevector is problem specific – **must fulfil all boundary conditions**
- Result is an **upper limit** for the ground state energy, likely to be close to actual ground state if trial wavevector is close to the actual eigenvector
- Easy to use, but **no information on how close the upper limit is to the actual energy**
- Derived wave function may bear no/little resemblance to actual wavefunction – **should not be used for calculating other measurables**

Variational particle in a box

Use the variational method to find an upper bound of the ground state energy for the 1D particle in a box using the trial wavefunction

$$\psi(x) = x(a - x)$$

- The Hamiltonian is

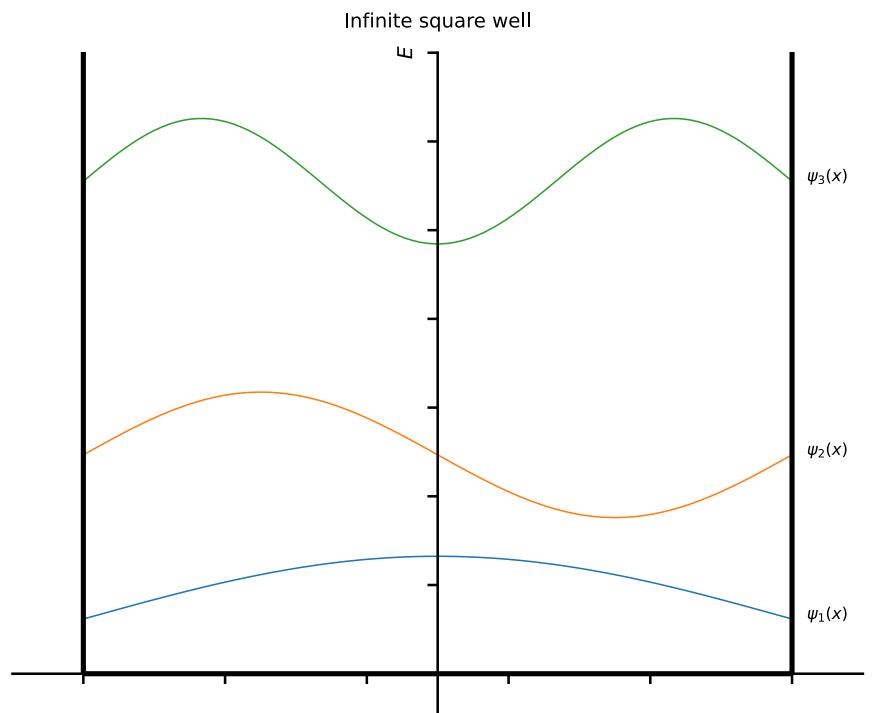
$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \text{ for } 0 \leq x \leq a$$

- Need to check if $\psi(x)$ is a good trial wavefunction

$$\psi(0) = \psi(a) = 0$$

- We need to evaluate

$$E_0 \leq \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$



Energy eigenfunctions of an infinite square well potential

Variational particle in a box

Normalise the wavefunction:

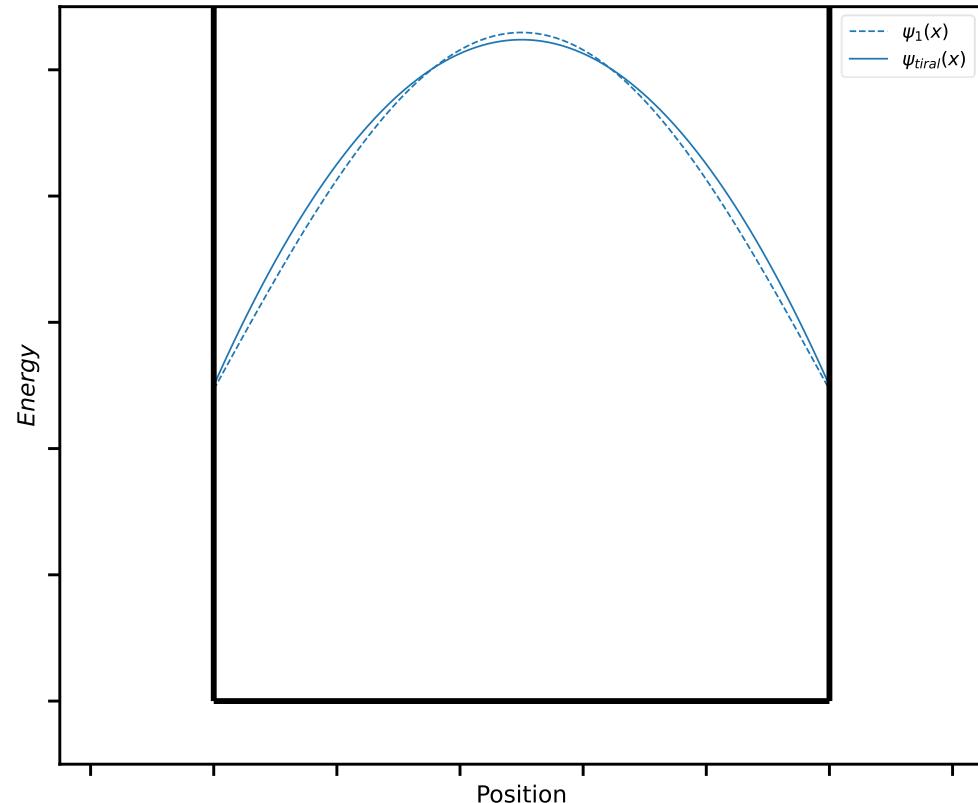
$$\psi(x) = \frac{\sqrt{30}}{a^{5/2}} x(a - x)$$

Compute $\langle \psi | H | \psi \rangle$:

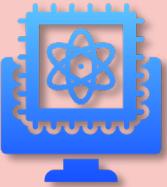
$$\begin{aligned} \int_0^a \psi^*(x) H \psi(x) dx &= -\frac{30\hbar^2}{2a^5 m} \int_0^a (ax - x^2) \frac{d^2}{dx^2} (ax - x^2) dx \\ &= \frac{30\hbar^2}{a^5 m} \int_0^a (ax - x^2) dx = \frac{5\hbar^2}{a^2 m} \end{aligned}$$

Compare this with $E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$:

$$\frac{\pi^2 \hbar^2}{2ma^2} \leq \frac{5\hbar^2}{a^2 m}$$



The exact energy eigenfunction and our trial wavefunction

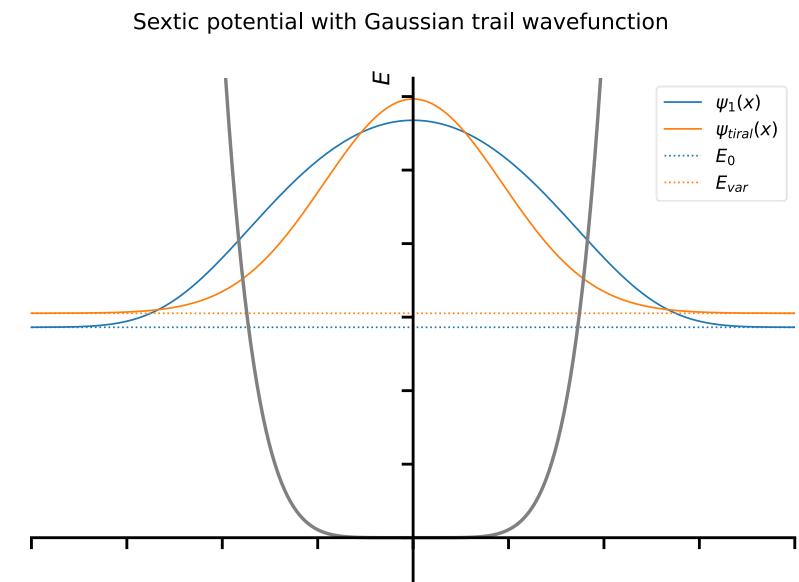


Non-trivial variational example

Approximate the ground state energy of the sextic potential $V(x) = \alpha x^6$ using the Gaussian trial wavefunction

$$\psi(x) = Ae^{-bx^2}$$

$$E_0 \leq \left(\frac{5\alpha\hbar^6}{18m^3} \right)^{1/4}$$



The exact energy eigenfunction and our trial wavefunction.

Note that $E_0 \leq \langle \psi_{trial} | H | \psi_{trial} \rangle$

The variational method: how to make it go?

The key to success is a good trial wave function

A good wavefunction will:

1. Conserve parity

Ask: is the wave function even or odd?

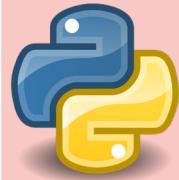
2. Model the asymptotic behaviour correctly

Ask: how does the wavefunction approach zero?

3. Be integrable

Ask: Does the integral converge? Numerical integration may be appropriate if analytic integration is not

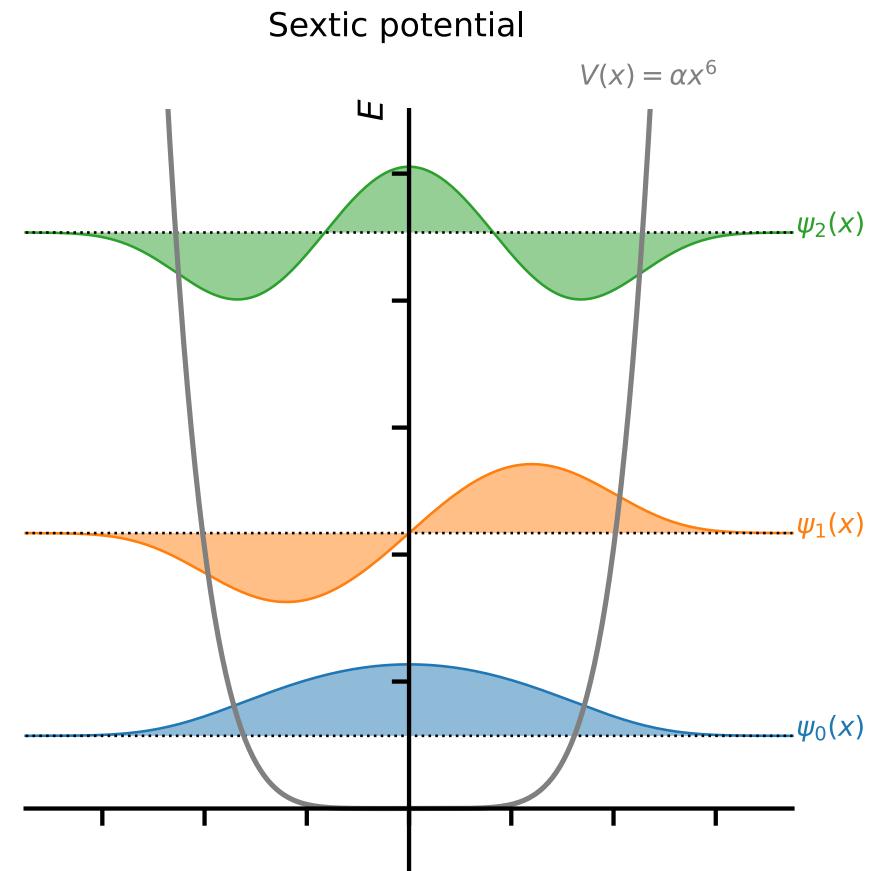
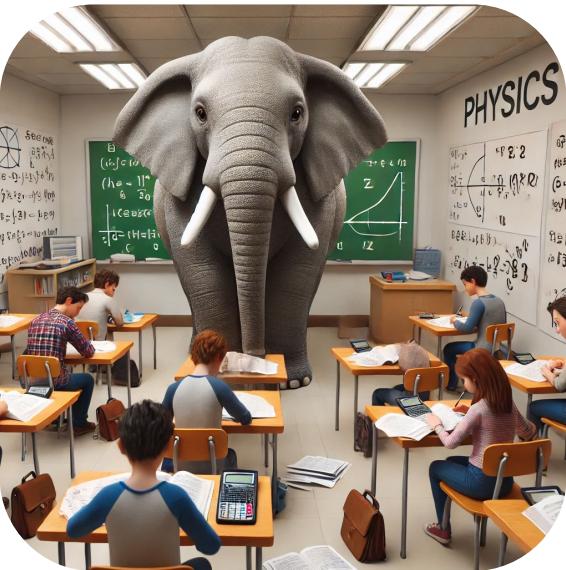




How to find energy eigenfunctions

I just showed a plot of the energy eigenfunction for the sextic potential, but how did I find this?

When discussing calculation methods:



Energy eigenstates for a sextic potential



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Summary

Problems

M10.10, M10.18, M10.19

- Perturbation theory
 - Useful when we can identify a solvable problem and incorporate additional small effects
 - “Similar” to Taylor expansion
 - Need to be careful with degenerate states
- The variational method
 - A tool for establishing an upper bound on energies
 - Can turn hard QM problems into easier linear algebra problems