ChemE 2200 - Physical Chemistry II for Engineers

Today:

Course Overview

Recap of Quantum Theory and Quantum Chemistry

The Quantum Description of the Hydrogen Atom

Defining Question:

Why does an electron not spiral into an atom's nucleus?

Reading for Today's Lecture:

Review the principles of quantum mechanics – Chp 4.

Review the quantum description of the hydrogen atom – Chp 6.

Reading for Quantum Lecture 2:

McQ & S – The H atom and multi-electron atoms – Chp 8.

Physical Chemistry II for Engineers

Syllabus:

Applied Quantum Chemistry
Classical Thermodynamics
Chemical Kinetics

Textbook:

Physical Chemistry: A Molecular Approach, Donald McQuarrie and John Simon (1997).

Optional Reference:

Problems & Solutions to Accompany McQuarrie & Simon's Physical Chemistry: A Molecular Approach, Heather Cox, Donald McQuarrie, and John Simon (1997).

Course Format

Lectures:

Read textbook in advance.

Review your notes after lecture – annotate.

Ask questions – in lecture, calculation sessions, and office hours.

Calculation Sessions:

Work exercises in ad hoc teams.

Solutions will be presented.

Homework:

Assigned weekly on Wednesday.

Will be complemented by Calculation Session exercises.

Homework will *not* be submitted.

Note:

Calculation Section *will* meet this week:

Wednesday at 2:30 p.m. in 245 Olin Hall.

Teaching Assistants

Lara Capellino

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Emily Destito

Vivian Liu

Amy Wu

Course Syllabus

Applied Quantum Chemistry:

The hydrogen atom and multi-electron atoms – atomic orbitals

Diatomic molecules – molecular orbitals

Interaction of Electromagnetic Radiation with Matter

Selection rules and absorption probability (overlap integrals).

Photon energy and associated molecular transition:
microwave (rotational), infrared (vibrational), visible/UV (electronic).

Strategic dissociation of molecules: photolithography, polymerization initiation (UV-curable epoxies such as dental fillings), selective heating of target molecules delivered to cancer cells

Electrons in Solids: insulators, conductors, and semiconductors.

Free electron theory and band theory.

Design of infrared detectors (night vision) and photovoltaics.

Course Syllabus, continued

Classical Thermodynamics:

Empirical; not based on microscopic (molecular) description.

Description of the Equilibrium State.

physical observables $\xrightarrow{\text{classical thermodynamics}}$ abstract quantities

P, V, T, N, and chemical identity $\longrightarrow$ U – internal energy (1st Law)

S – entropy (2nd Law)

Conversions of Energy: Heat – thermal equilibrium

Work – mechanical equilibrium

Chemical Reaction – $2H_2 + CO \rightarrow CH_3OH$

Physical Reaction – liquid $\rightarrow$ gas

Course Syllabus, continued

Chemical Kinetics:

Molecular bonding and interaction of radiation (photons) with matter
from quantum chemistry.

Given chemical concentrations and *T*, calculate reaction rate;
Calculate rate of conversion between thermodynamic equilibrium states.

Given equation for rate of reaction, ascertain molecular mechanism
of conversion between thermodynamic equilibrium states.

Derive molecular basis for chemical kinetics from –
Kinetic Theory of Gases,
Transition State Theory, and
Potential Energy Surfaces.

Physical Chemistry II for Engineers

Part 1. Applied Quantum Chemistry

Chp. 6: The Hydrogen Atom (review)

Chp. 8: Multi-electron Atoms – Atomic Orbitals

Chp. 9: Diatomic Molecules – Molecular Orbitals

Chp.13: Molecular Spectroscopy

- Microwave
- Infrared
- Visible/UV
- X-ray

Chp. 15: Lasers and Photochemistry

Handout: Electrons in Solids – Metals, Insulators, and Semiconductors

Quantum Chemistry Recap

(A) Quantum Theory – *The Concepts*

Matter and radiation exist at discrete energies: particles and photons are quantized.

The position and momentum of a particle
cannot be simultaneously known exactly.

Everything is simultaneously both a particle and a wave.

Observing a particle's state (position and momentum) affects the particle's state.

Although a 'theory,' it is not tenuous. Quantum theory passes two critical tests:

1. Internal consistency

2. Explains and predicts experimental observations.

There are no known conflicts, although
quantum theory may be incomplete.

e.g., the Einstein-Podolsky-Rosen (EPR) Paradox

"I think I can safely say that nobody really understands quantum mechanics."
Richard Feynman

Quantum Chemistry Recap, continued

(B) Quantum Mechanics – *The Mathematical Formalism*

A quantum system is described by a wavefunction, $\Psi(x, y, z, t)$.

The wavefunction, Ψ, is an eigenfunction of Schrödinger's Equation,
$H\,\Psi = E\,\Psi$ such that the energy is an eigenvalue.

The probability distribution is given by $\Psi\Psi^*$.

Classical mechanics is deterministic; Quantum mechanics is probabilistic.

The certainty of linear momentum and position are limited by the Heisenberg Uncertainty Principle: $(\Delta p)(\Delta x) \geq \hbar/2$.

Physical quantities – linear momentum, angular momentum, kinetic energy, potential energy, and position – are eigenvalues of their corresponding operator: $\hat{A}\Psi = a\Psi$.

Probability of absorption and emission of a photon of electromagnetic radiation is given by the overlap integral $< \Psi_{initial}| \mathbf{r} | \Psi_{final}>$.

Quantum Chemistry Recap, continued

(C) Quantum Chemistry – *Application to Chemical Systems*

Atomic structure – electron orbitals

Molecular structure – bonding

The interaction of electromagnetic radiation with matter

Analysis – spectroscopy

Selective heating – microwave ovens

Selective bond breaking – photochemistry

Quantum Chemistry – Why Bother?

(A) Practical

electron configuration $\longrightarrow$ bonding $\longrightarrow$ chemical reactions

Behavior at the atomic level determines behavior at the macroscopic level.

Classical mechanics fails at the atomic level.

Classical mechanics predicts electrons should spiral into the nucleus.

Quantum mechanics prohibits the collapse of the universe.

Classical mechanics predicts spontaneous combustion of organic matter.

Quantum mechanics predicts O_2 is relatively unreactive.

Quantum mechanics is required to explain -

Why CO_2 is a greenhouse gas, but O_2 and N_2 are not.

Why O_3 blocks UV radiation, but O_2 and N_2 do not.

Why a diamond is clear, but silicon is opaque.

How a laser functions.

How to design a photovoltaic material.

Quantum Chemistry – Why Bother?

(A) Intellectual

Quantum theory and relativity are the most important scientific revolutions of the 20th century.

The two great conceptual advances of our understanding of nature:

Matter is composed of atoms

Periodic properties of the elements

Stoichiometry

Atoms behave differently than the macroscopic world.

Quantum Weirdness:

A particle can simultaneously exist in two places.

A particle can move from one location to another location without ever existing between the two locations.

A particle can escape from a box by vanishing inside the box and appearing outside the box.

A particle can *briefly* have negative kinetic energy, such that $(\Delta E)(\Delta t) \geq \hbar/2$

Quantum Chemistry – Why a Reputation for Difficult?

Quantum chemistry calculates only two simple quantities:

Where is the particle?

How fast is it moving?

Simple questions, but strange answers.

Compare to the quantities of thermodynamics:

Energy. There is no definition of energy. There are only lists of forms of energy.

Entropy. What is that?

"Those who are not shocked when they first come across quantum theory could not possibly have understood it."

Niels Bohr - Nobel Prize for Quantum Theory and Atomic Structure (1922)

"I am going to describe something which is different from anything you know about. It will be difficult. But the difficulty really is psychological and exists in the perpetual torment 'But how can it be like that?' which is an uncontrolled but utterly vain desire to see it in terms of something familiar."

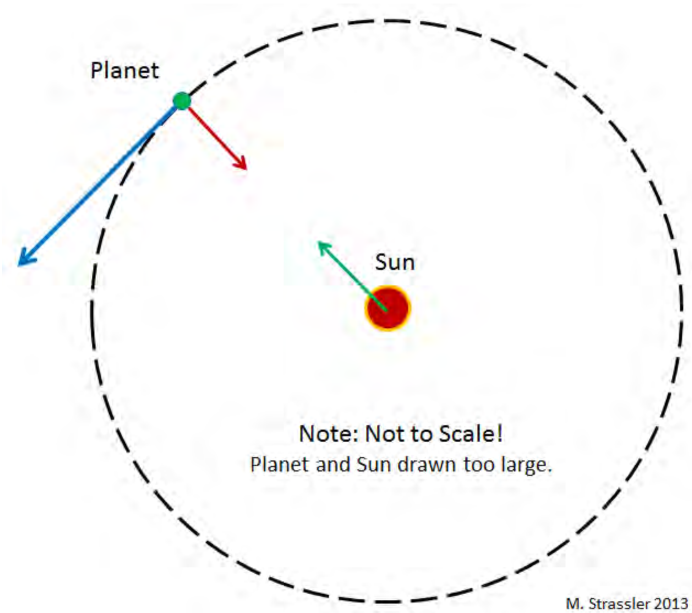
Richard Feynman - Nobel Prize for Quantum Electrodynamics (1965)

Quantum phenomena have no macroscopic analogies.   None

The Hydrogen Atom – a proton and an electron

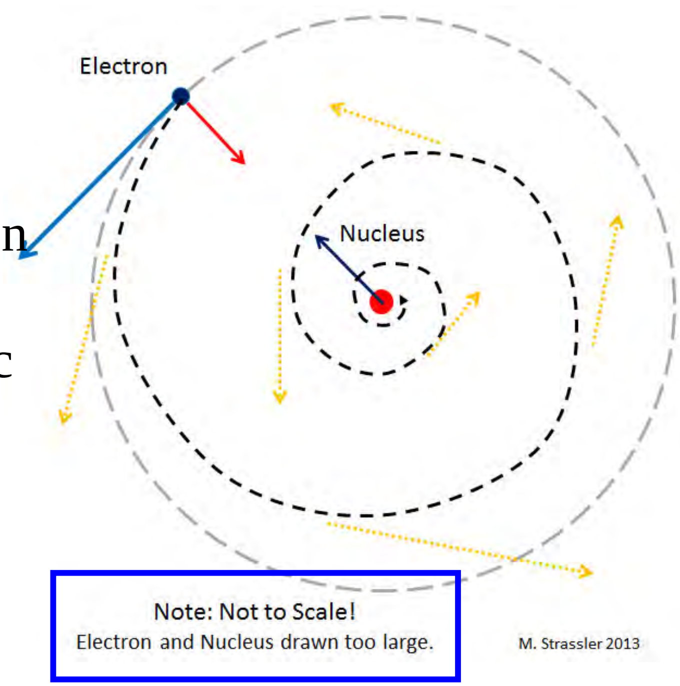
Classical Mechanics Description

Gravitational attraction



Electrostatic attraction

Classical mechanics: an accelerating charged particle (the magnitude or the direction of its velocity changes with time) radiates electromagnetic waves.



Electron emits photons and decreases kinetic energy, and ultimately collapses into the nucleus.

If the hydrogen atom were the size of Bailey Hall,

the nucleus would be the the size of a pin head.

The Quantum Mechanical Description of the Hydrogen Atom

The first topic of Quantum Chemistry.

Our Goals:

The chemical properties of atoms: bonding to form molecules

The interaction of radiation with matter: spectroscopy, sensors, and photochemistry

We seek $\Psi_{\text{H atom}}$.

We must solve $\hat{H}\Psi_{\text{H atom}} = E\Psi_{\text{H atom}}$

$$\hat{H} = -\frac{\hbar^2}{2m_{\text{nucleus}}}\nabla^2_{\text{nucleus}} - \frac{\hbar^2}{2m_{\text{electron}}}\nabla^2_{\text{electron}} - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right)$$

kinetic energy of the nucleus

kinetic energy of the electron

electrostatic attraction

Transform to a center-of-mass system.

$$\hat{H} = \boxed{-\frac{\hbar^2}{2m_{\text{total}}}\nabla^2_{\text{com}}}\ \boxed{-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right)}$$

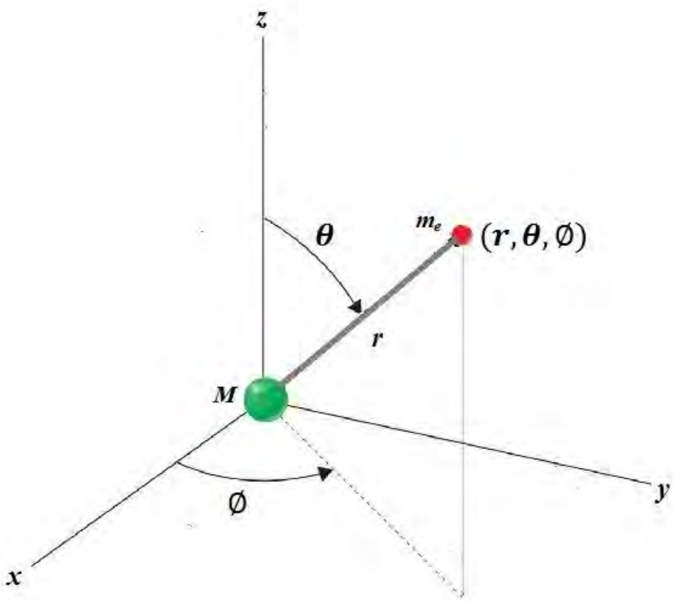
$$m_{\text{total}} = m_{\text{nucleus}} + m_{\text{electron}} \approx m_{\text{nucleus}}$$

$$\mu = \frac{m_{\text{nucleus}} + m_{\text{electron}}}{m_{\text{nucleus}} m_{\text{electron}}} \approx m_{\text{electron}}$$

linear motion of the H atom

Motion of nucleus and electron relative to center of mass

The Quantum Mechanical Description of the Hydrogen Atom



$$\left(\boxed{-\frac{\hbar^2}{2\mu}\nabla_r^2}\boxed{-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right)}\right)\psi = E\psi(r,\theta,\phi)$$

kinetic energy — potential energy

In spherical coordinates,

$$\left(\boxed{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\boxed{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}\right]}\boxed{-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right)}\right)\psi = E\psi(r,\theta,\phi)$$

rigid rotator – see McQ & S p. 175

$$\left(-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]\boxed{+\frac{\hbar^2}{2\mu r^2}\hat{L}^2}\boxed{-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right)}\right)\psi = E\psi(r,\theta,\phi)$$

the spherical harmonics

$$\hat{L}^2\psi = EY(\theta,\phi)$$

$$= \frac{\ell(\ell+1)}{2I}\hbar^2 Y(\theta,\phi)$$

$$\left(-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right]\boxed{\boxed{+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}}\boxed{-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right)}}\right)\psi = ER(r)Y(\theta,\phi)$$

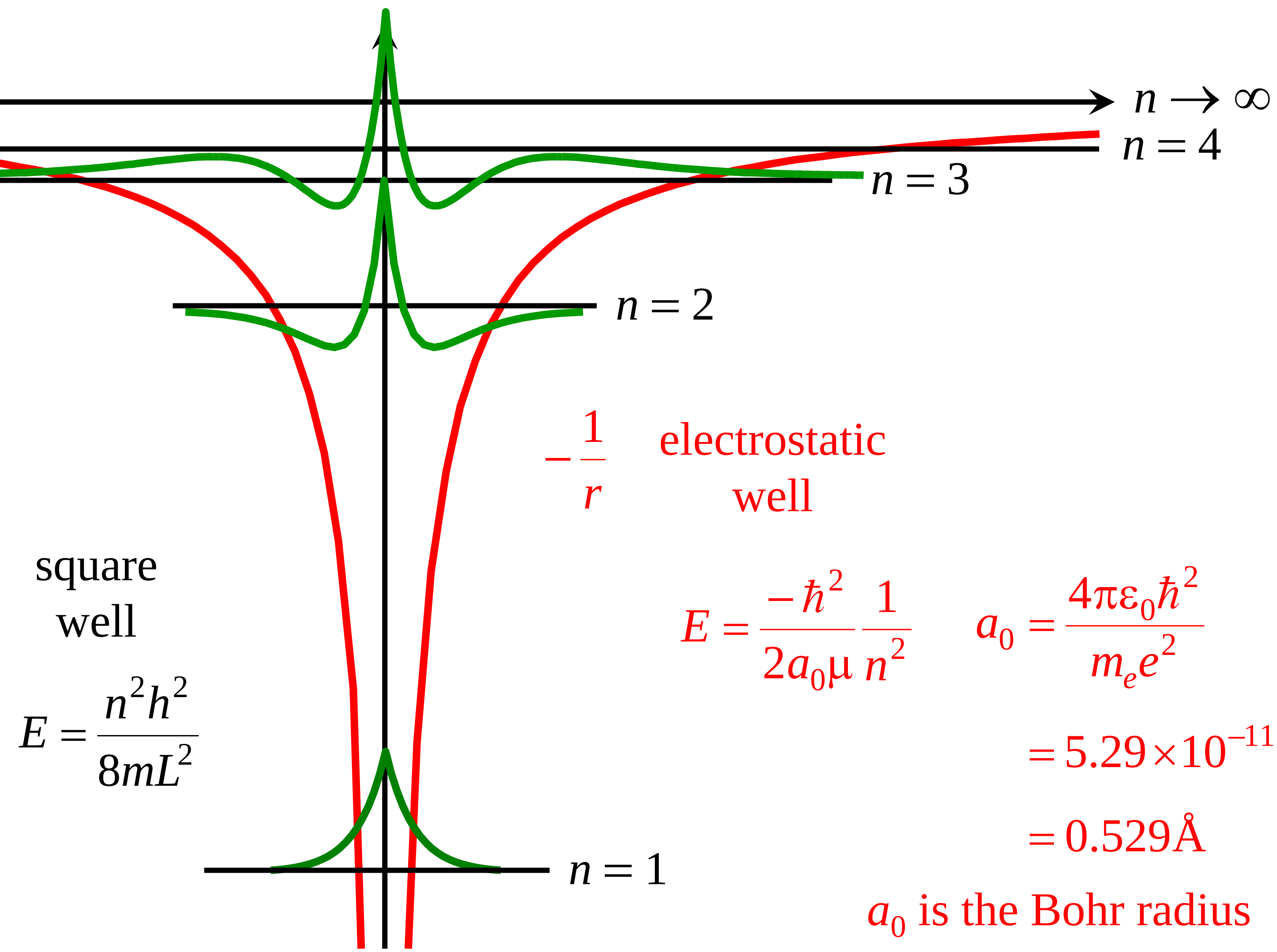
total potential

The Hydrogen Atom Potential

centripetal force $\boxed{\dfrac{\hbar^2\ell(\ell+1)}{2\mu}\left(\dfrac{1}{r^2}\right)}\boxed{-\dfrac{e^2}{4\pi\varepsilon_0}\left(\dfrac{1}{r}\right)}$ electrostatic force

Consider no angular momentum, $\ell = 0$

Electron and nucleus move on a linear path towards each other.



$-\dfrac{1}{r}$ electrostatic well

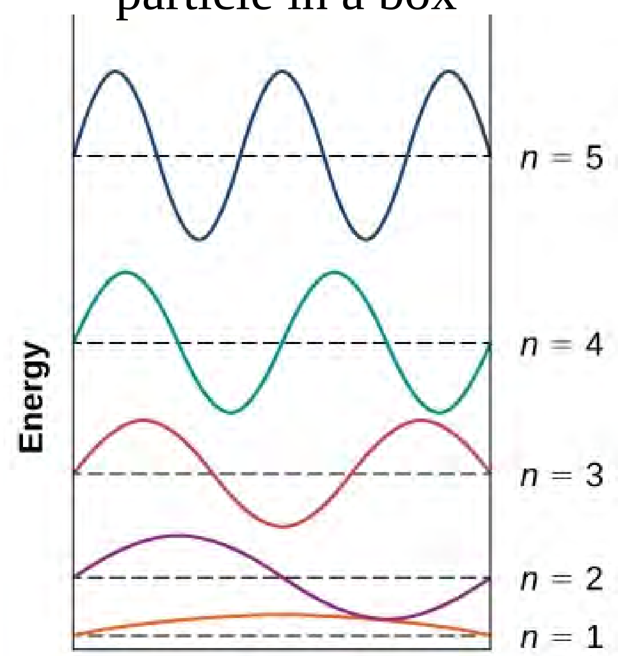
$$E = \frac{-\hbar^2}{2a_0\mu}\frac{1}{n^2} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

$$= 5.29\times10^{-11}\,\mathrm{m}$$

$$= 0.529\,\text{Å}$$

a_0 is the Bohr radius

particle in a box



square well

$$E = \frac{n^2h^2}{8mL^2}$$

The Hydrogen Atom – The s Orbitals

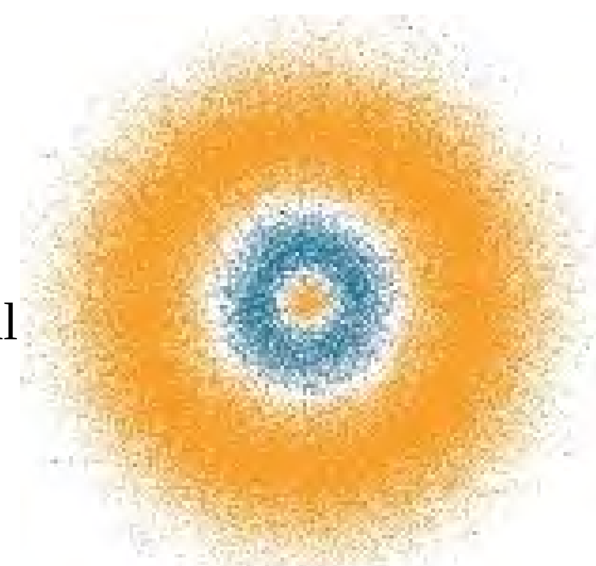
Electron orbitals with zero angular momentum are the s orbitals.

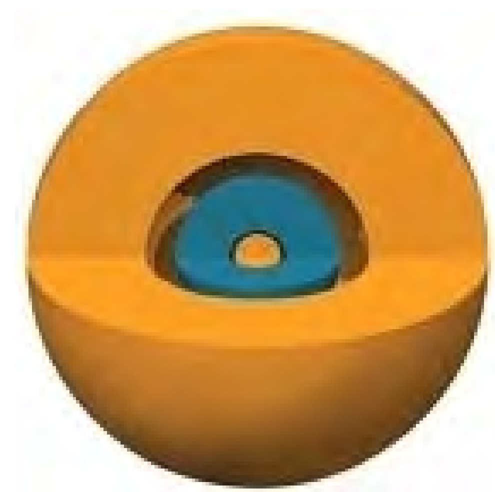
electron cloud | electron contour

$n = 1$
The 1s orbital

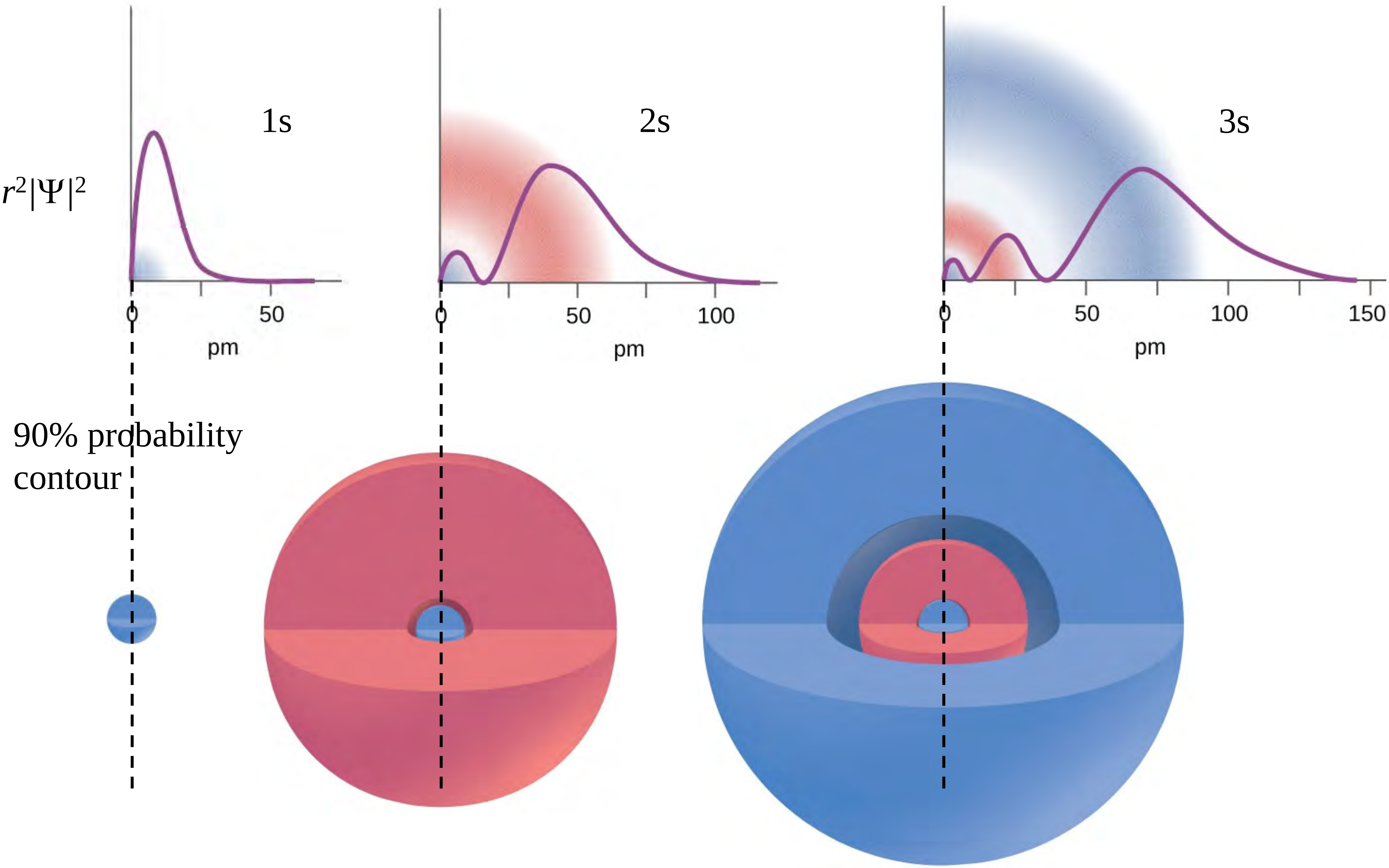
$n = 2$
The 2s orbital

$n = 3$
The 3s orbital





The Hydrogen Atom – The s Orbitals

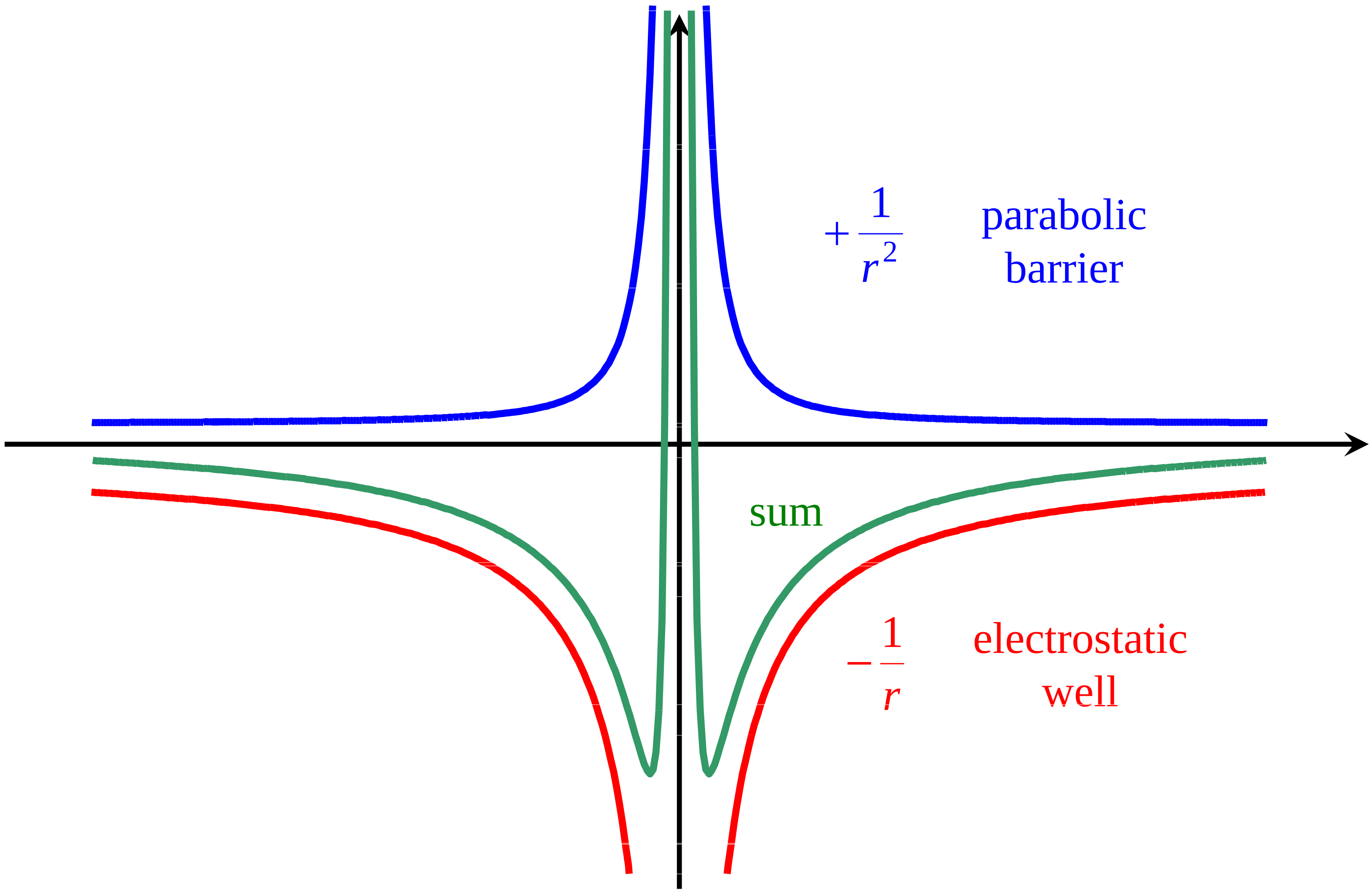


The Hydrogen Atom Potential

centripetal force $\boxed{\frac{\hbar^2 \ell(\ell+1)}{2\mu}\left(\frac{1}{r^2}\right)}\boxed{-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r}\right)}$ electrostatic force

Consider finite angular momentum, $\ell \neq 0$

Electron rotates aroung the nucleus.



The Hydrogen Atom Potential

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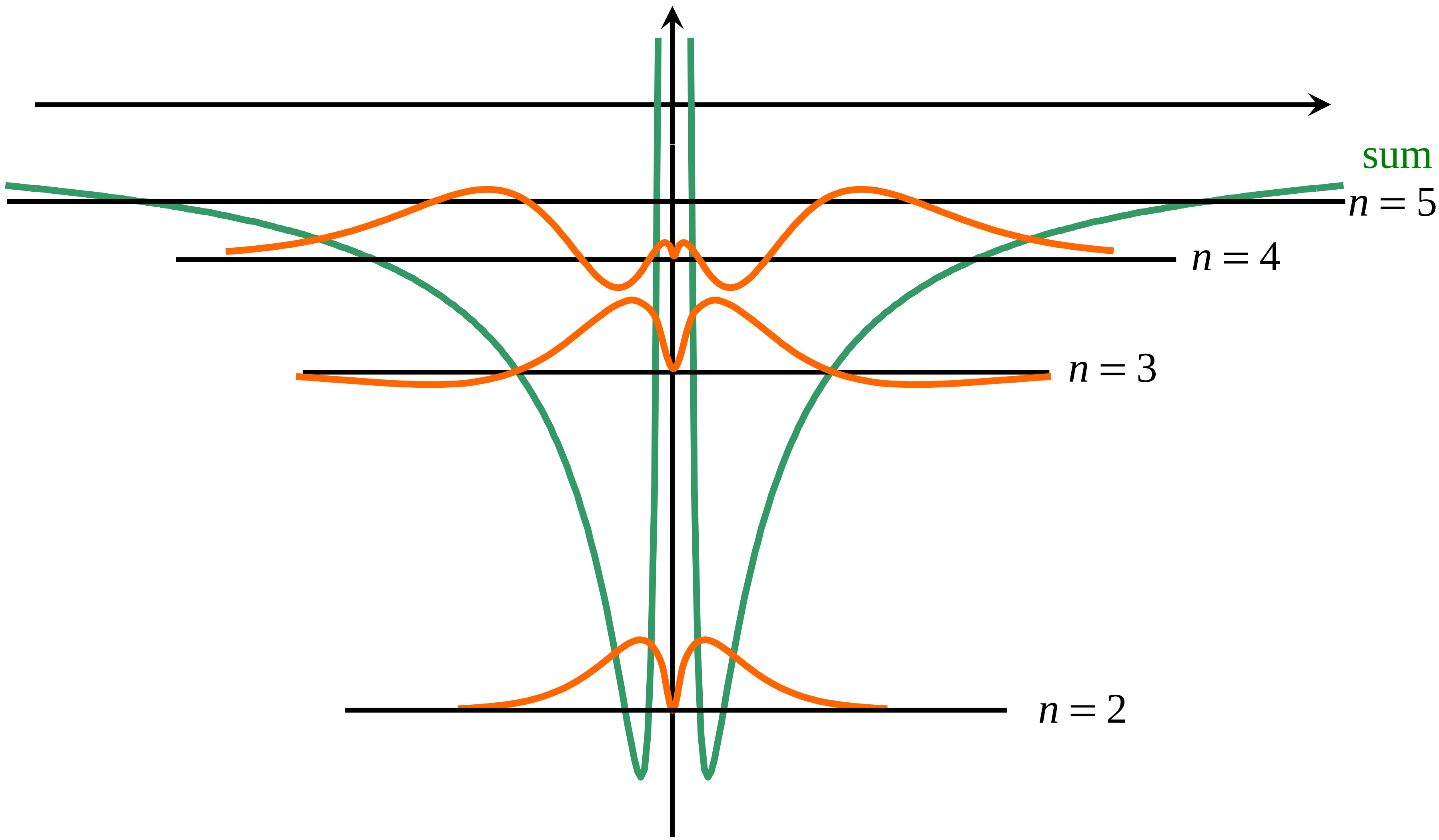
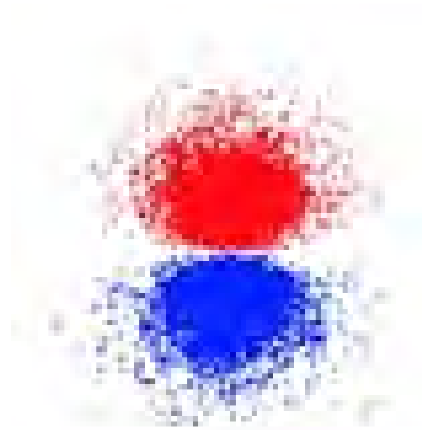
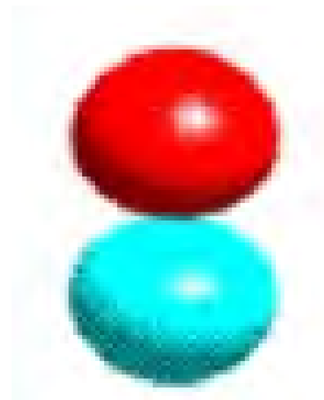


The Hydrogen Atom – The p Orbitals

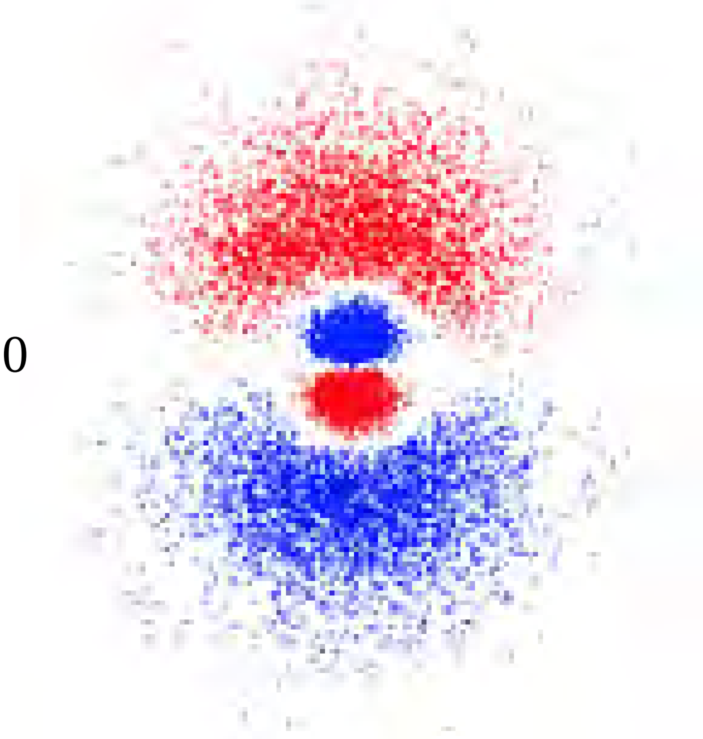
electron cloud | electron contour

n = 2, l = 1, m_l = 0
The $2p_z$ orbital



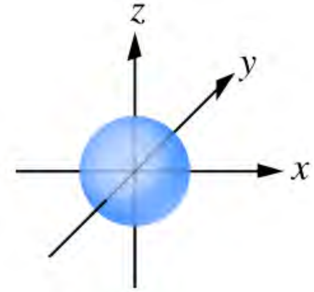


n = 3, l = 1, m_l = 0
The $3p_z$ orbital



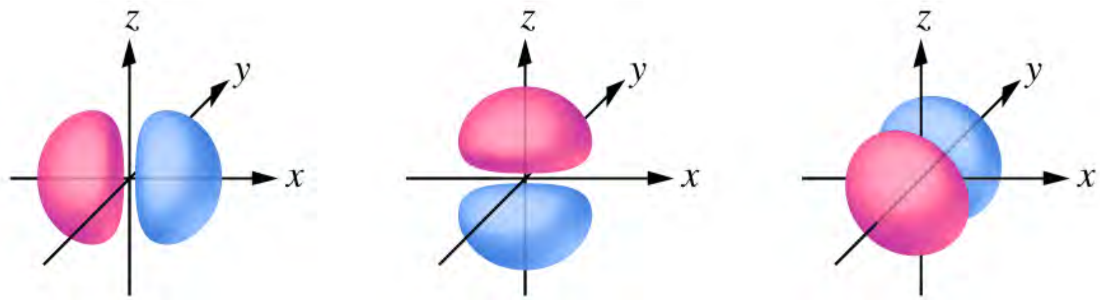
The Hydrogen Atomic Orbital Shapes

$n = 1$, $l = 0$, $m_l = 0$



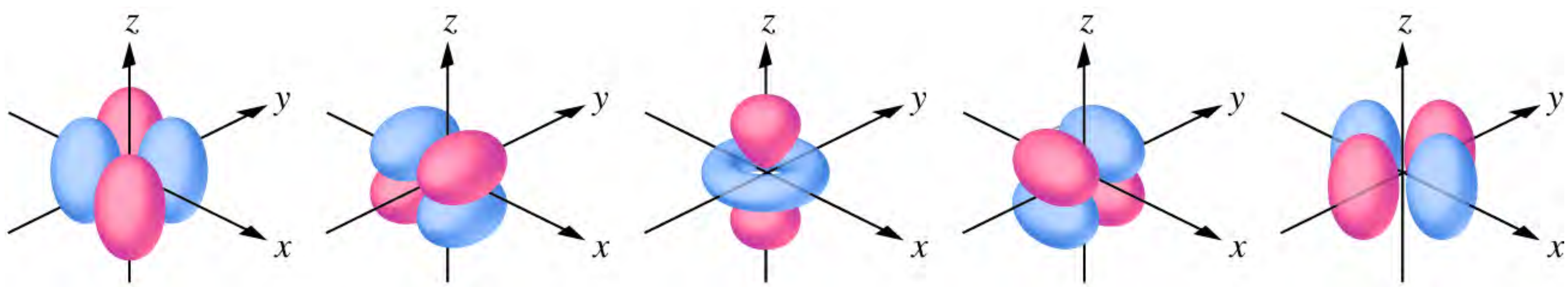
1s

$n = 2$, $l = 1$, $m_l = 1, 0, –1$

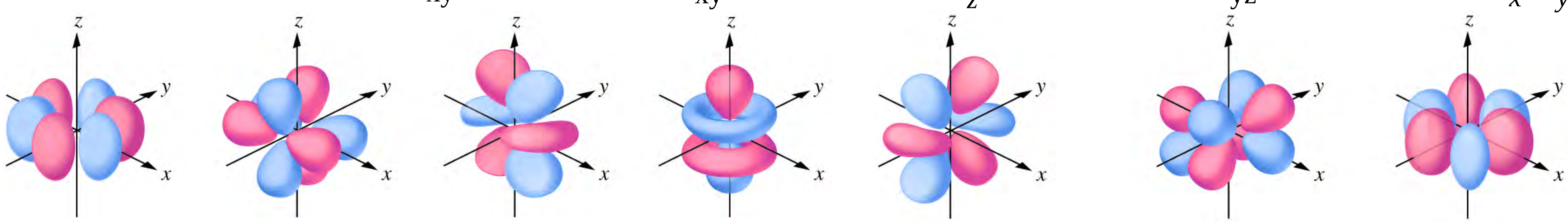


$2p_x$, $2p_z$, $2p_y$

$n = 3$, $l = 2$,
$m_l = 2, 1, 0, –1, –2$



$3d_{xy}$ $3d_{xy}$ $3d_{z^2}$ $3d_{yz}$ $3d_{x^2-y^2}$



$n = 4$, $l = 3$, $m_l = 3, 2, 1, 0, –1, –2, –3$

The Hydrogen Atomic Orbital Expressions

n is the principal quantum number.

$n = 1, 2, 3, \ldots$

l is the orbital angular momentum.

$l = 0, 1, 2, \ldots, n-1$

m_l is the z-projection of the orbital angular momentum.

$m_l = -l, -l+1, \ldots, 0, l-1, l$

$$E = \frac{-\hbar^2}{2a_0\mu}\frac{1}{n^2}$$

$n=1,$	$l=0,$	$m=0$	$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n=2,$	$l=0,$	$m=0$	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma)e^{-\sigma/2}$
	$l=1,$	$m=0$	$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\cos\theta$
	$l=1,$	$m=\pm 1$	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta\cos\phi$
			$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta\sin\phi$
$n=3,$	$l=0,$	$m=0$	$\psi_{3s} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (27-18\sigma+2\sigma^2)e^{-\sigma/3}$
	$l=1,$	$m=0$	$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\cos\theta$
	$l=1,$	$m=\pm 1$	$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\sin\theta\cos\phi$
			$\psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\sin\theta\sin\phi$
	$l=2,$	$m=0$	$\psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}(3\cos^2\theta-1)$
	$l=2,$	$m=\pm 1$	$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta\cos\phi$
			$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta\sin\phi$
	$l=2,$	$m=\pm 2$	$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta\cos 2\phi$
			$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta\sin 2\phi$

$$\sigma = \frac{Zr}{a_0}$$

Z is the nuclear charge

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

$$= 5.29\times 10^{-11}\,\text{m}$$

$$= 0.529\,\text{Å}$$

a_0 is the Bohr radius

Table 6.6 from McQuarrie & Simon, p. 218.