REVIEW OF QUANTUM MECHANICS AND ATOMIC PHYSICS

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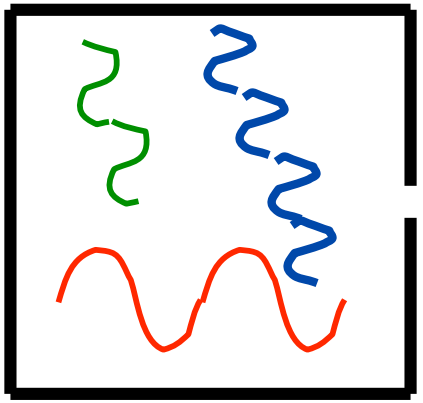
REVIEW OF QUANTUM MECHANICS AND ATOMIC PHYSICS

1. Who needs Quantum Mechanics?
2. The basic formalism: wave functions, operators
3. Energy, position, momentum, angular momentum,and their measurements.
4. The Schrödinger Equation, harmonic oscillator, hydrogen atom
5. Atomic Structure

1. Who needs Quantum Mechanics?

Blackbody radiation



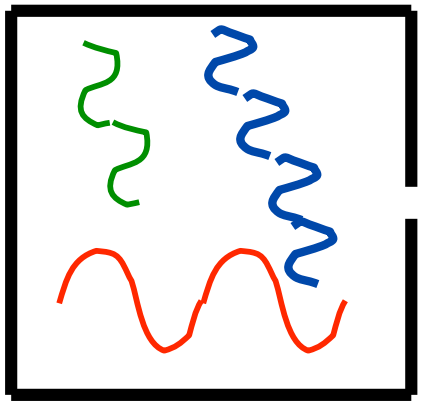
Classical physics: at temperature T every mode has average energy (1/2) $k_B T$

Number of modes between ν , $\nu+d\nu$ with $k_x = 2n\pi/L$, etc.

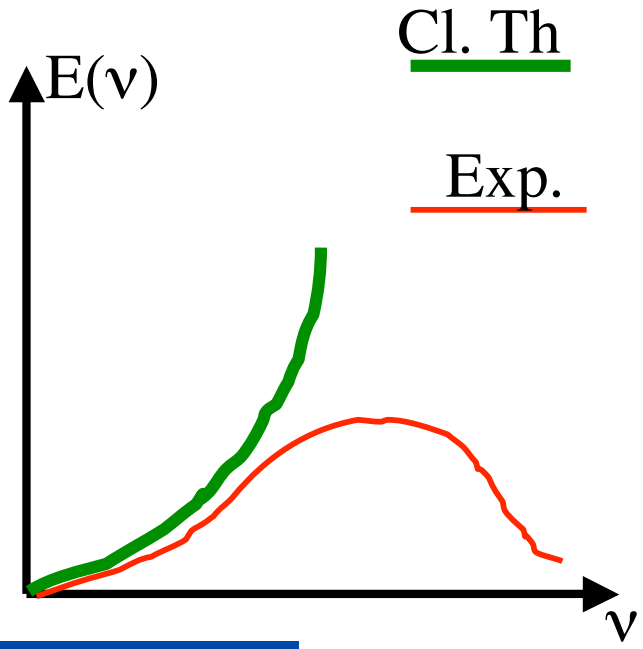
$$(V/c^3)\, 8\pi\nu^2\, d\nu$$

Total Energy at temp. T $\sim T \int_0^\infty \nu^2 d\nu = \infty$!!

Blackbody radiation



Energy in modes between ν , ν+dν:



Planck: Walls exchange energy with field at frequency ν only in quanta:

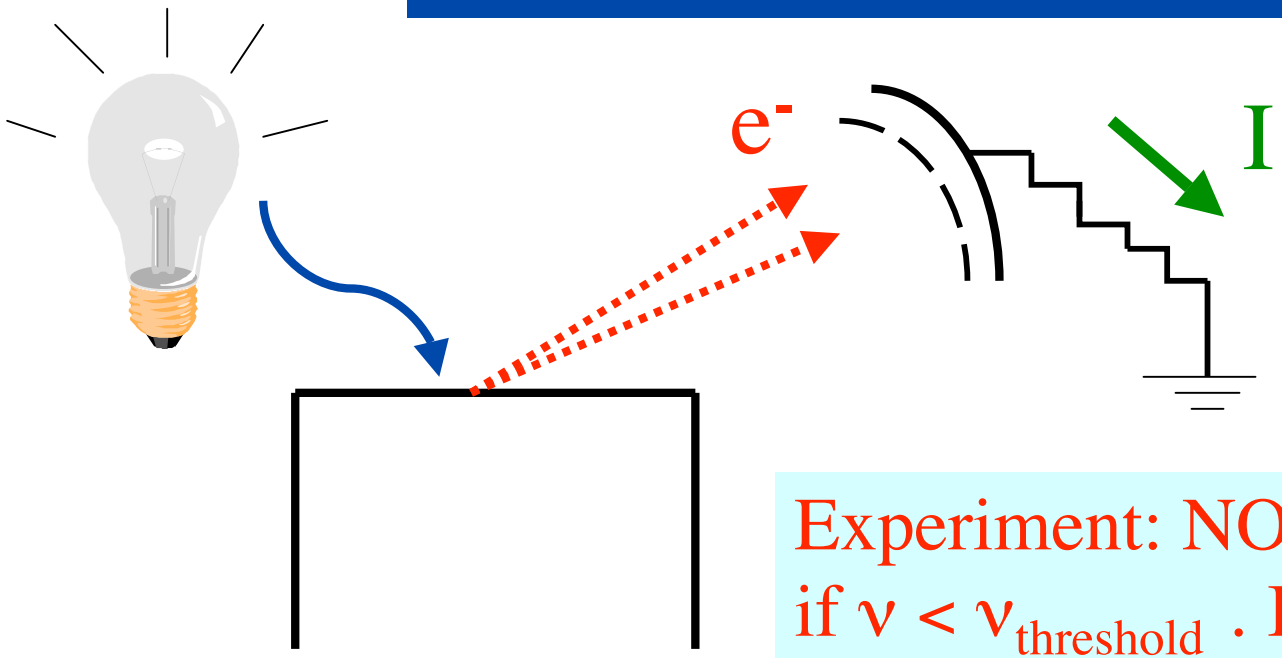
hν, 2hν, 3hν, 4hν, ...

Planck's constant:

$$h = 6.6252 \cdot 10^{-27} erg \cdot s$$

$$\hbar = h/2\pi = 1.0544 \cdot 10^{-27} erg \cdot s$$

PHOTOELECTRIC EFFECT

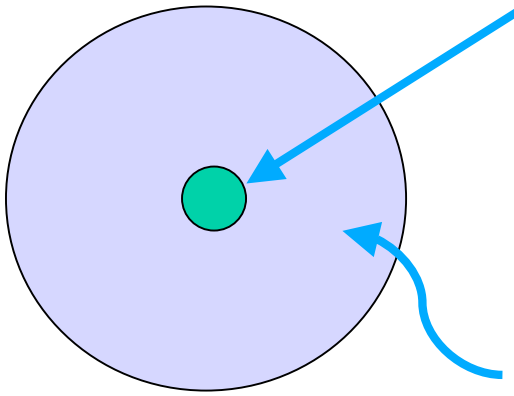


Experiment: NO photoelectrons if $\nu < \nu_{threshold}$. Intensity of light determines intensity of photocurrent, but not electron energy. Electron kinetic energy depends only on ν !

Einstein (1905): $E = h\nu$

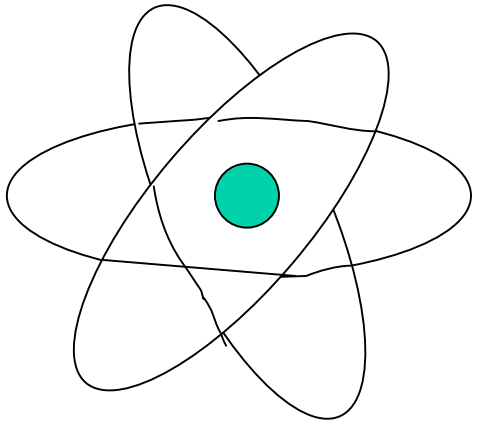
STABILITY OF "PLANETARY" ATOMS

Rutherford's α−particles scattering experiments show:



Nucleus with charge +Ze

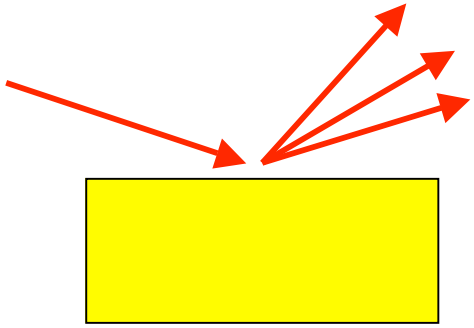
Z electrons each with charge -e

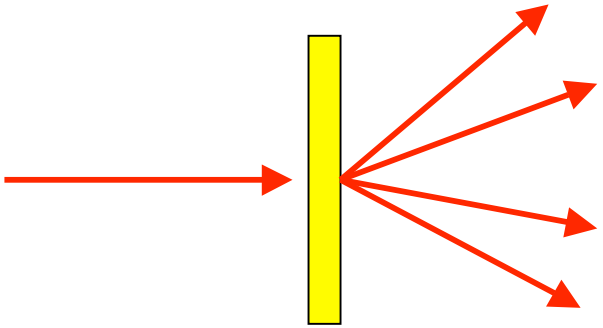


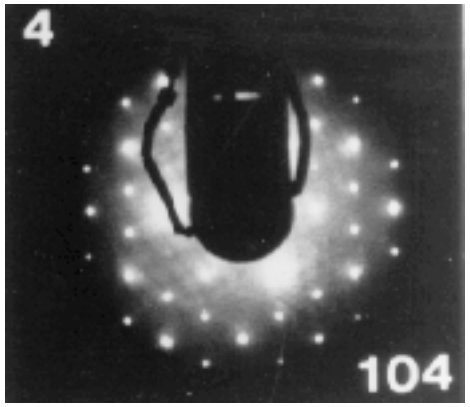
" Planetary" model of the atom

Why electrons do not radiate and fall into the nucleus??

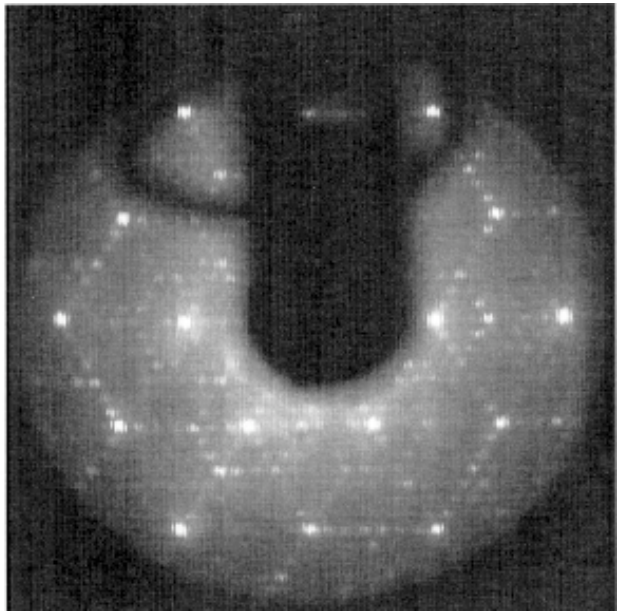
Electrons are waves, because they are diffracted by crystals and crystal surfaces!







Ag 100



Si 111 7X7

2. The basic formalism: wave functions, operators.

In *classical* physics the state of a particle at a given time is specified by the value of its position r(t) and its velocity v(t) (or momentum p(t)).

More generally for a system of N particles the state is identified by giving $r_i(t)$, $p_i(t)$, with i =1,2,…N.

In *quantum* physics the state of a particle at a given time is specified by a complex wavefunction of its coordinates,

$$\psi(x,y,z,t).$$

Physical interpretation: $|\psi(x,y,z,t)|^2$ dxdydz proportional to probability that a measurement at time t will find particle between x,y,z, and x+dx,y+dy, z+dz.

2. The basic formalism: wave functions, operators, measurement

Note that $|\psi(x,y,z,t)|^2\,dxdydz$ is equal - and not just proportional to the probability if:

$$\int |\psi(x,y,z,t)|^2\, dxdydz = 1$$

For a system of N particles, generalize:

$\psi(x,y,z,t) \Rightarrow \psi(x_1,y_1,z_1;\ x_2,y_2,z_2;\ldots;\ x_N,y_N,z_N;\ t)$

Related to prob. of finding one particle between r_1 and $r_1+d\,r_1$, one between r_2 and $r_2+d\,r_2$, etc.

Observable physical quantites:

e.g. the *position* x,y,z of a particle;

the *momentum* p_x, p_y, p_z, of a particle ;

the *z component of its angular momentum* l_z ;

its *energy* E

the *total momentum* $\mathbf{P} = \Sigma\, \mathbf{p}_i$ of a system of particles.

In Quantum Mechanics observables correspond to *linear*, *self-adjoint* (or *hermitian*) operators in the vector space of wavefunctions

Definition:

Operator Ô: $\hat{O}\,\psi(x,y,z) = \psi_1(x,y,z)$; **it operates (performs an operation) on the wavefunction $\psi(x,y,z)$ that transforms it into a different function $\psi_1(x,y,z)$.**

Examples of Operators:

$\frac{\partial}{\partial x}$: $\hat{O}\,\psi(x,y,z) = \frac{\partial}{\partial x}\,\psi(x,y,z)$
$e^{i\varphi}$: $\hat{O}\,\psi(x,y,z) = e^{i\varphi}\,\psi(x,y,z)$
$x\frac{\partial}{\partial y}$: $\hat{O}\,\psi(x,y,z) = x\frac{\partial}{\partial y}\,\psi(x,y,z)$

Definitions:

Linear operator:

$\hat{O}\,[c_1\,\psi_1(x,y,z) + c_2\,\psi_2(x,y,z)] = c_1\,\hat{O}\,\psi_1(x,y,z) + c_2\,\hat{O}\,\psi_2(x,y,z)$

Scalar product of two wavefunctions:

$$\langle \psi_1 \mid \psi_2 \rangle = \int \psi_1^*(x,y,z)\psi_2(x,y,z)\,dxdydz$$

Self-adjoint or hermitian operator :

An operator $\hat{O}$ such that for two arbitrary functions

$$\langle \psi_1 \mid \hat{O}\psi_2 \rangle = \langle \hat{O}\psi_1 \mid \psi_2 \rangle = \langle \psi_1 \mid \hat{O} \mid \psi_2 \rangle$$

$$\int \psi_1^*(x,y,z)\left\{\hat{O}\psi_2(x,y,z)\right\}dxdydz = \int \left\{\hat{O}\psi_1(x,y,z)\right\}^* \psi_2(x,y,z)\,dxdydz$$

Examples of hermitian operators:

$\hat{O} = x_0$ (a real multiplicative constant)

$\hat{O} = x$ (the operator that transforms ψ into $x\psi$).

$\hat{O} = i\frac{\partial}{\partial x}$ (For functions that vanish at infinity, proof uses integration by parts)

3. Energy, position, momentum, angular momentum,…and

their measurement

Examples of correspondence between observables and operators:

Position along x [or y, z] $\hat{O}\,\psi(x,y,z) = x\,\psi(x,y,z)$ *[or* $y\psi$, $z\psi$ *]*

Momentum component p_x : $\hat{O}\psi(x,y,z) = -i\hbar\dfrac{\partial}{\partial x}\psi(x,y,z)$

Kinetic energy of a particle with mass *m* , $T=(p_x^2 + p_y^2 + p_x^2)/2m$:

$$\hat{O}\psi(x,y,z) = \frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z)$$

$$\nabla^2\psi(x,y,z) = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)$$

Examples of correspondence between observables and operators

Angular momentum of a particle, $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$:

$$L_x = (yp_z - zp_y): \quad -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\psi(x,y,z)$$

$$L_y = (zp_x - xp_z): \quad -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\psi(x,y,z)$$

$$L_z = (xp_y - yp_x): \quad -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi(x,y,z)$$

Remarks on products of operators and commutation

$L_x = (yp_z - zp_y)$ → $-i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})\psi(x,y,z)$

We implicitly used the notion of operator product, e.g. yp_z as the operator that first applies p_z to ψ, than applies (i.e. multiplies by) y to the resulting function.

Operator product is non-commutative, in general:

$$\hat{A}\hat{B}\psi(x,y,z) \neq \hat{B}\hat{A}\psi(x,y,z)$$

Example:

$$xp_x\psi = x(-i\hbar\frac{\partial}{\partial x}\psi) = -i\hbar x\frac{\partial}{\partial x}\psi$$

$$p_x x\psi = -ih\frac{\partial}{\partial x}(x\psi) = -i\hbar\psi - i\hbar x\frac{\partial}{\partial x}\psi$$

Commutator: $[x, p_x] = xp_x - p_x x = i\hbar$

Eigenvalues and eigenvectors of linear operators

Definition:

$\psi_n(x,y,z)$ is an ***eigenvector*** (eigenfunction) of linear operator $\hat{O}$ with **eigenvalue** e_n (e_n is a number) if, for all x,y,z:

$$\hat{O}\,\psi_n(x,y,z) = e_n\,\psi_n(x,y,z)$$

Example:

$$\hat{O} = p_z = -i\hbar\frac{\partial}{\partial z}$$

Eigenvector

$$\psi(x,y,z) = \varphi(x,y)e^{ik_z z}$$

Eigenvalue

$$\hat{p}_z\,\varphi(x,y)e^{ik_z z} = \hbar k_z \varphi(x,y)e^{ik_z z}$$

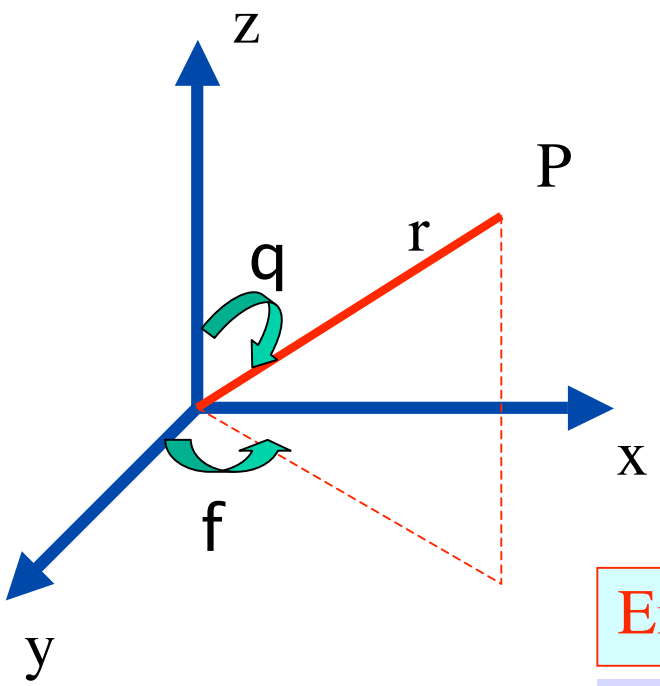
Generalization: $e^{i\vec{k}\cdot\vec{r}} = e^{ik_x x} e^{ik_y y} e^{ik_z z}$

Is an eigenvector of: $\mathbf{p_x, p_y, p_z}$

with eigenvalues respectively: $\hbar k_x, \hbar k_y, \hbar k_z$

….and also of: $\hat{T} = \frac{p^2}{2m} = \frac{-\hbar^2 \nabla^2}{2m}$

With eigenvalue: $\frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$



$$\hat{O} = L^2 = L_x^2 + L_y^2 + L_z^2$$

Spherical Harmonic

Eigenfunctions: $\psi(x,y,z) = c(r)\, Y_{\ell,m}(\theta,\phi)$

$$L^2\chi(r)Y_{l,m}(\theta,\varphi) = l(l+1)\hbar^2\chi(r)Y_{l,m}(\theta,\varphi)$$

$l=0,1.2,3,\ldots;$ $\quad m=-l,-(l-1),\ldots\ldots l-1,l$

The same $c(r)\, Y_{\ell,m}(\theta,\phi)$ are also eigenfunctions of L_z:

$$L_z\chi(r)Y_{l,m}(\theta,\varphi) = m\hbar\chi(r)Y_{l,m}(\theta,\varphi)$$

Operators that commute have common eigenfunctions!

$$[L^2, L_z] = 0$$

The spherical harmonics (l=0,1,2)

ℓ	m_ℓ	$Y_{\ell m_l}(\theta,\phi) = \Theta_{\ell m_l}(\theta)\Phi_{m_l}(\phi)$
0	0	$(1/4\pi)^{1/2}$
1	0	$(3/4\pi)^{1/2}\cos\theta$
1	± 1	$\mp(3/8\pi)^{1/2}\sin\theta e^{\pm i\phi}$
2	0	$(5/16\pi)^{1/2}(3\cos^2\theta - 1)$
2	± 1	$\mp(15/8\pi)^{1/2}\sin\theta\cos\theta e^{\pm i\phi}$
2	± 2	$(15/32\pi)^{1/2}\sin^2\theta e^{\pm 2i\phi}$

$$\Phi_{m\ell}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_\ell \phi}$$

$$\Theta_{\ell m_\ell}(\theta) = \left[\frac{2\ell+1}{2}\frac{(\ell - m_\ell)!}{(\ell + m_\ell)!}\right]^{1/2} P_\ell^{m_\ell}(\theta)$$

$P_\ell^{m_\ell}(\theta) = associated\ \ Legendre\ \ polynomial$

Measurements of Observables in QM

If a system is in a state described by a wavefunction which is an eigenfunction of an operator $\hat{O}$, with eigenvalue e, then measurements of the observable shall always produce the value e.

If on the other hand the system is in a state described as a linear superposition of the eigenfunctions of $\hat{O}$, $\psi_n(x,y,z)$ with eigenvalues e_n, i.e.:

$$\psi(x,y,z) = \sum_n c_n \psi_n(x,y,z)$$

Then the measurement of $\hat{O}$ can produce any of the e_n values, with a probability equal to:

$$P(e_n) = \frac{|c_n|^2}{\sum_{n'} |c_{n'}|^2}$$

Measurements of Observables in QM

Before the measurement the wavefunction is:

$$\psi(x,y,z) = \sum_n c_n \psi_n(x,y,z)$$

After the measurement, with result e_n it becomes:

$$\psi_n(x,y,z)$$

Three Important Theorems

Theorem 1. *All eigenvalues of a hermitian operator are real*

Theorem 2. *Eigenfunctions of the same operator corresponding to two different eigenvalues are orthogonal, i.e.*

$$\hat{O}\psi_1 = e_1\psi_{`1}, \hat{O}\psi_2 = e_2\psi_{`2}$$

$$e_1 \neq e_2$$

imply: $\langle \psi_1 | \psi_2 \rangle = 0$

Theorem 3. *Eigenfunctions* ψ_n *of a hermitian operator are a complete set, i.e. an arbitrary function* $\psi(x,y,z)$ *can be written as:*

$$\psi(x,y,z) = \sum_n c_n \psi_n(x,y,z)$$

4. The Schrödinger Equation and the Role of Energy

In *classical* physics a particle moving in an external potential V(x,y,z) has a Hamiltonian (energy written as a function of position and momentum) given by:

$$H = \frac{p^2}{2m} + V(x, y, z)$$

The corresponding *quantum mechanical* operator is:

$$\hat{H} = \hat{T} + \hat{V} = \frac{-\hbar^2 \nabla^2}{2m} + V(x, y, z),$$

where $\hat{V}\psi(x, y, z) = V(x, y, z)\psi(x, y, z)$, (a multiplicative op.)

Energy plays a very important role: it determines the time evolution of systems.

(Time-dependent) Schrödinger Equation:

$$i\hbar\frac{\partial}{\partial t}\psi(x,y,z,t) = \hat{H}\psi(x,y,z,t)$$

Suppose that at t=0 (x,y,z,0) is an eigenvector of H^:

$$\hat{H}\psi(x,y,z,0) = E_n\psi(x,y,z,0)$$

(Time independent) Schrödinger Equation

Then, at t=0:

$$i\hbar[\frac{\partial}{\partial t}\psi(x,y,z,t)]_{t=0} = \hat{H}\psi(x,y,z,0) = E_n\psi(x,y,z,0)$$

Solution:

$$\psi(x,y,z,t) = \psi(x,y,z,0)e^{-i(E_n/\hbar)t}$$

Consequence: for energy eigenfunctions, time dependence is just a *phase factor*, and:

$$|\psi(x,y,z,t)|^2 = |\psi(x,y,z,0)|^2$$

Probability distribution is **constant** in time: energy eigenfunctions are called **"stationary states".**

Time-independent Schrödinger Equation for Central Potentials

General motion of a particle in 3-dim. potential:

$$\hat{H}\psi(x,y,z) = [-\frac{\hbar^2\nabla^2}{2m} + V(x,y,z)]\psi(x,y,z) = E\psi(x,y,z)$$

Important class of potentials are those with with rotation invariance, i.e. depending only on distance from a centre:

$$V(x,y,z) = V(\sqrt{x^2 + y^2 + z^2}) = V(r)$$

Examples:

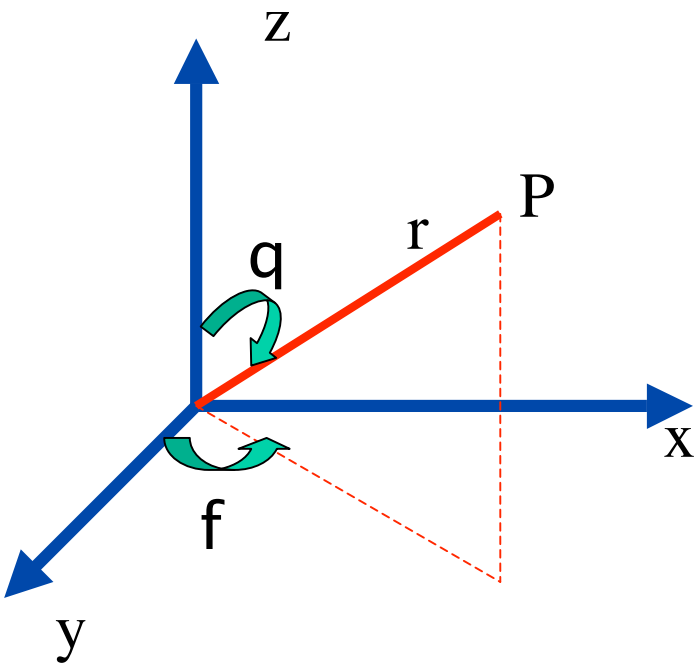
Coulomb potential $V(r) = -Z e^2/r$

3-dim. isotropic harmonic oscillator $V(r) = (1/2)\, m\, \omega^2 r^2$

General Structure of Solutions for Central Potentials

Solutions labelled by 3 numbers n,l,m: $\hat{H}\psi_{nlm} = E\psi_{nlm}$

To describe ψ_{nlm} (x,y,z) use spherical coordinates ψ_{nlm} (r,θ,ϕ):



Then: $\psi_{nlm}(r,\theta,\phi) = f_{nl}(r)\, Y_{lm}(\theta,\phi)$

n, principal quantum number

$\hat{L}$

$l(l+1)\hbar^2$

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

$\hat{L}_z$

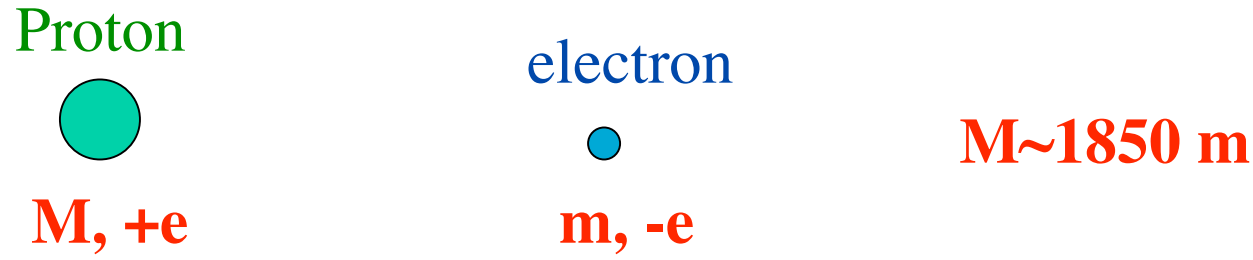
$m\hbar$

$m = -l, -(l-1), \ldots l-1, l$

"Radial Equation":

$$[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}]rf_{nl}(r) = E_{nl}rf_{nl}(r)$$

A two-body central force problem: the H atom



$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_P^2 - \frac{\hbar^2}{2m}\nabla_e^2 - \frac{e^2}{|\vec{r}_P - \vec{r}_e|}$$

Centre of Mass and Relative Coordinates:

$$\frac{M\vec{r}_P + m\vec{r}_e}{M+m}; \vec{r} = \vec{r}_P - \vec{r}_e; \frac{1}{m^*} = \frac{1}{M} + \frac{1}{m} \approx \frac{1}{m}$$

$$\hat{H} = -\frac{\hbar^2}{2(M+m)}\nabla_R^2 - \frac{\hbar^2}{2m^*}\nabla_r^2 - \frac{e^2}{r} = \hat{H}_R + \hat{H}_r$$

Free particle motion of the whole atom

Relative motion

A two-body central force problem: the H atom

$$(\hat{H}_R + \hat{H}_r)\Psi(\vec{R},\vec{r}) = E\Psi(\vec{R},\vec{r})$$

$$\Psi(\vec{R},\vec{r}) = \Phi(\vec{R})\psi(\vec{r})$$

Φ: Free particle motion of the whole atom:

$$\Phi(\vec{R}) = e^{i\vec{K}\cdot\vec{R}}; E_R = \frac{\hbar^2}{2(M+m)}K^2$$

ψ: Relative motion around the c. of m.:

$$\psi(\vec{r}) = \psi_{nlm}(\vec{r}) = f_{nl}(r)Y_{l,m}(\theta,\varphi)$$

A two-body central force problem: the H atom

Rydberg Constant, 13.6 eV

Energy levels:

E< 0 **n=1,2,3,…**

(bound) **l=0,1,2….n-1**

m=-l,-(l-1)….,l

$$E = -\frac{me^4}{2\hbar^2}\frac{1}{n^2}$$

E>0 **n=ik**

(ionized) **l=0,1,2…**

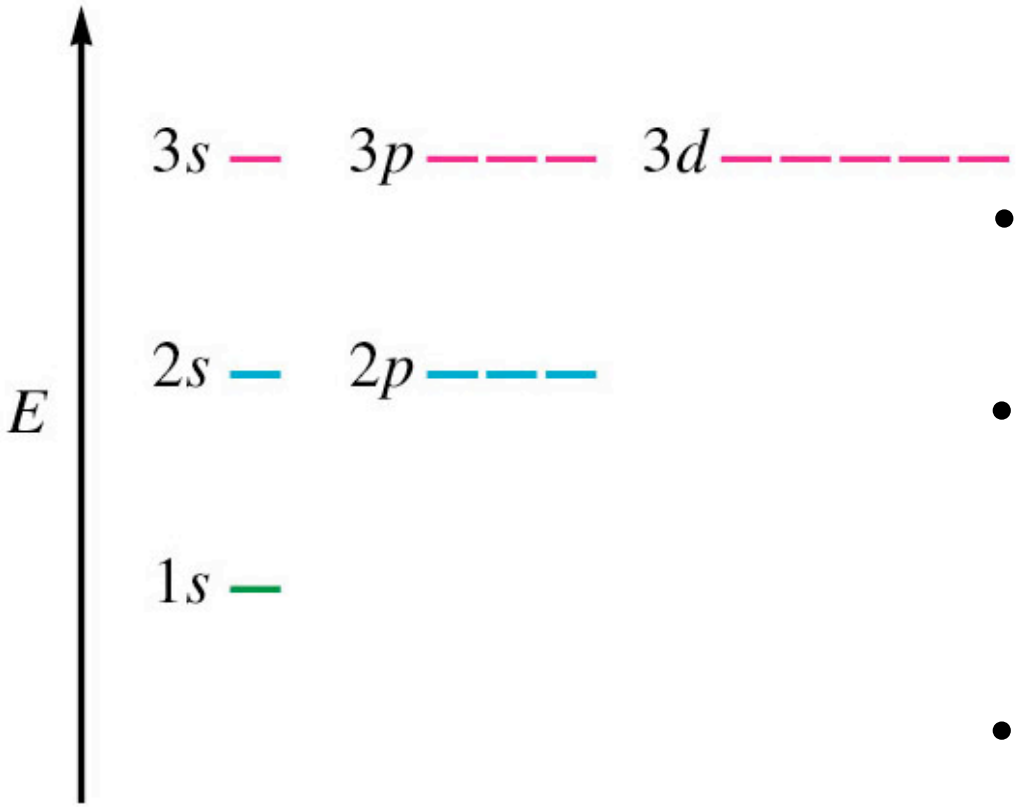
m=-l,-(l-1)….,l

$$E = \frac{\hbar^2 k^2}{2m^*}$$

Quantum Numbers and Orbitals

n	l	Orbital	m	# of Orb.
1	0	1s	0	1
2	0	2s	0	1
2	1	2p	-1, 0, 1	3
3	0	3s	0	1
3	1	3p	-1, 0, 1	3
3	2	3d	-2, -1, 0, 1, 2	5

Orbital Energies



- energy increases as $1/n^2$
- orbitals of same n, but different l are of equal energy ("degeneracy").
- the "ground" or lowest energy orbital is the 1s.

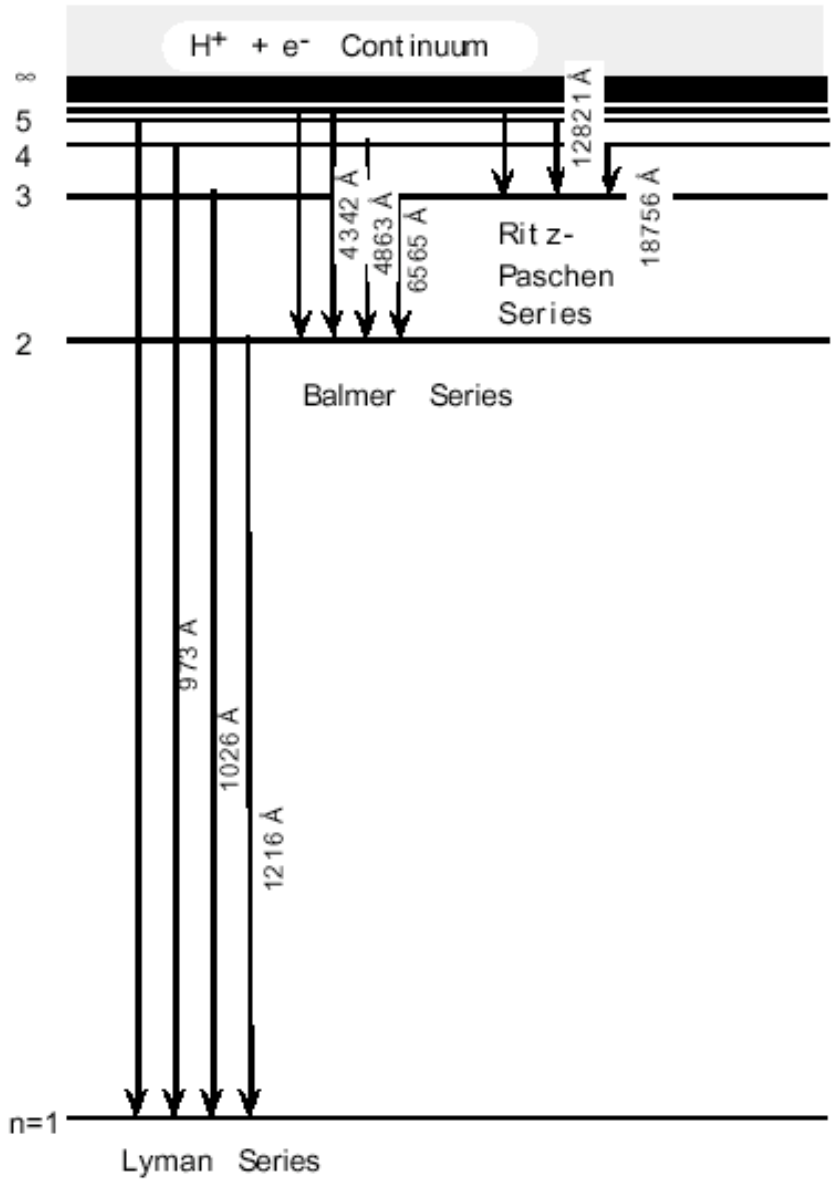
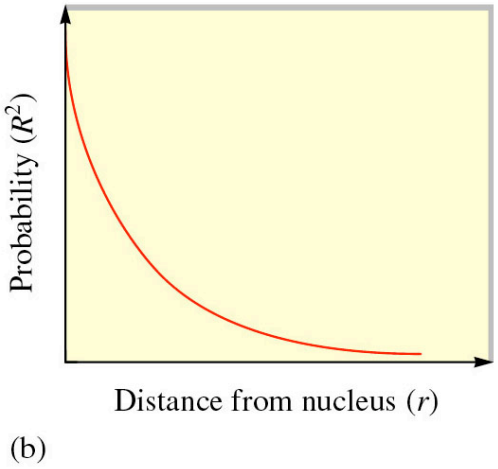


Fig 1. A few electronic energy levels of the hydrogen atom. As n increases the energy levels converge to a limit, and above this limit (the shaded area) there are a continuum of levels corresponding to complete separation of proton and electron with kinetic energy > 0

Orbital Shapes

- Note that the "1s" wavefunction has no angular dependence (i.e., θ and ϕ do not appear).



$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-\frac{Z}{a_0}r} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-\sigma}$$

Bohr radius

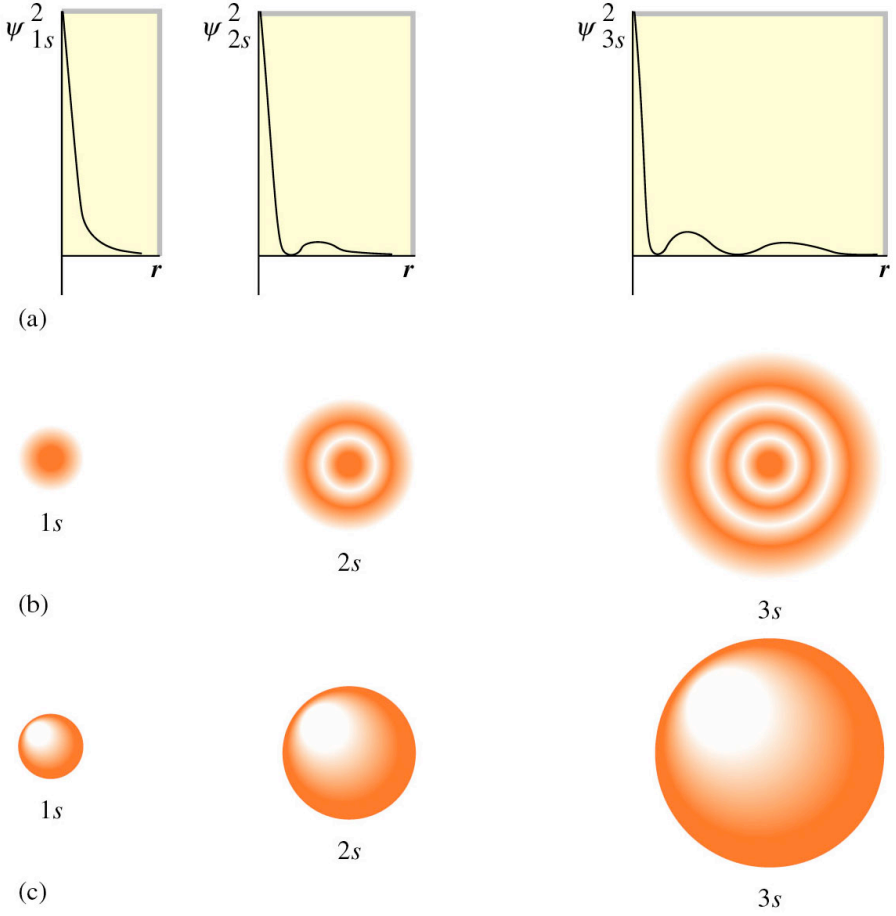
$$a_0 = \frac{\hbar^2}{me^2} = 0.539 \cdot 10^{-8}\, cm$$

Probability = $\psi^* \psi$

- Probability is spherical

Orbital Shapes (cont)

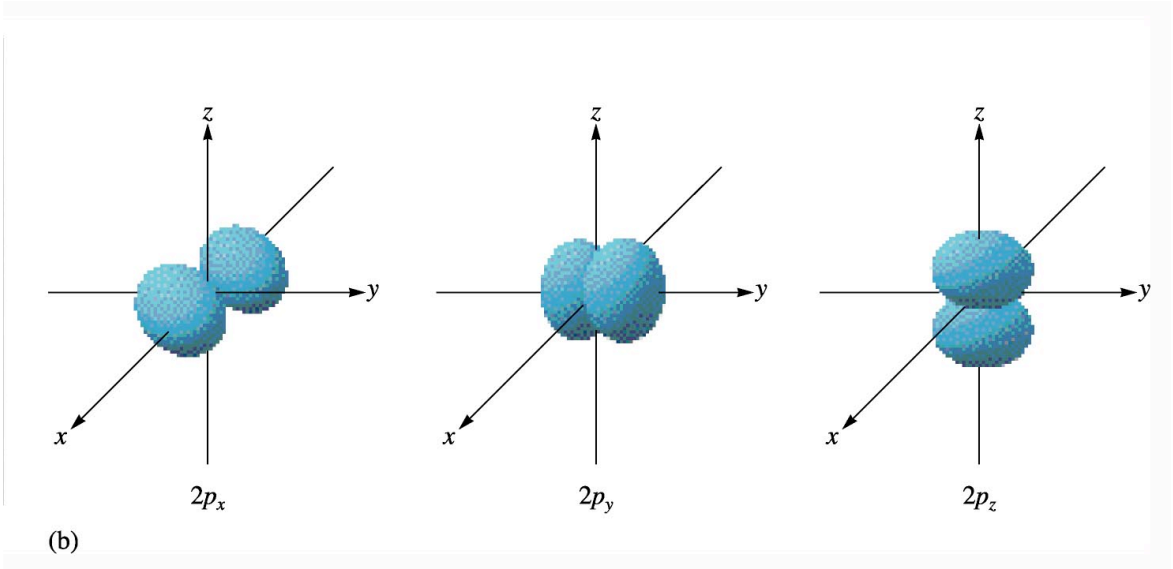
s (l = 0) orbitals



- r dependence only
- as n increases, orbitals demonstrate n-1 nodes.

Orbital Shapes (cont.)

2p (l = 1) orbitals



- not spherical, but lobed. $\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{3/2} \sigma e^{-\sigma/2} \cos\theta$
- labeled with respect to orientation along x, y, and z.

Orbital Shapes (cont.)

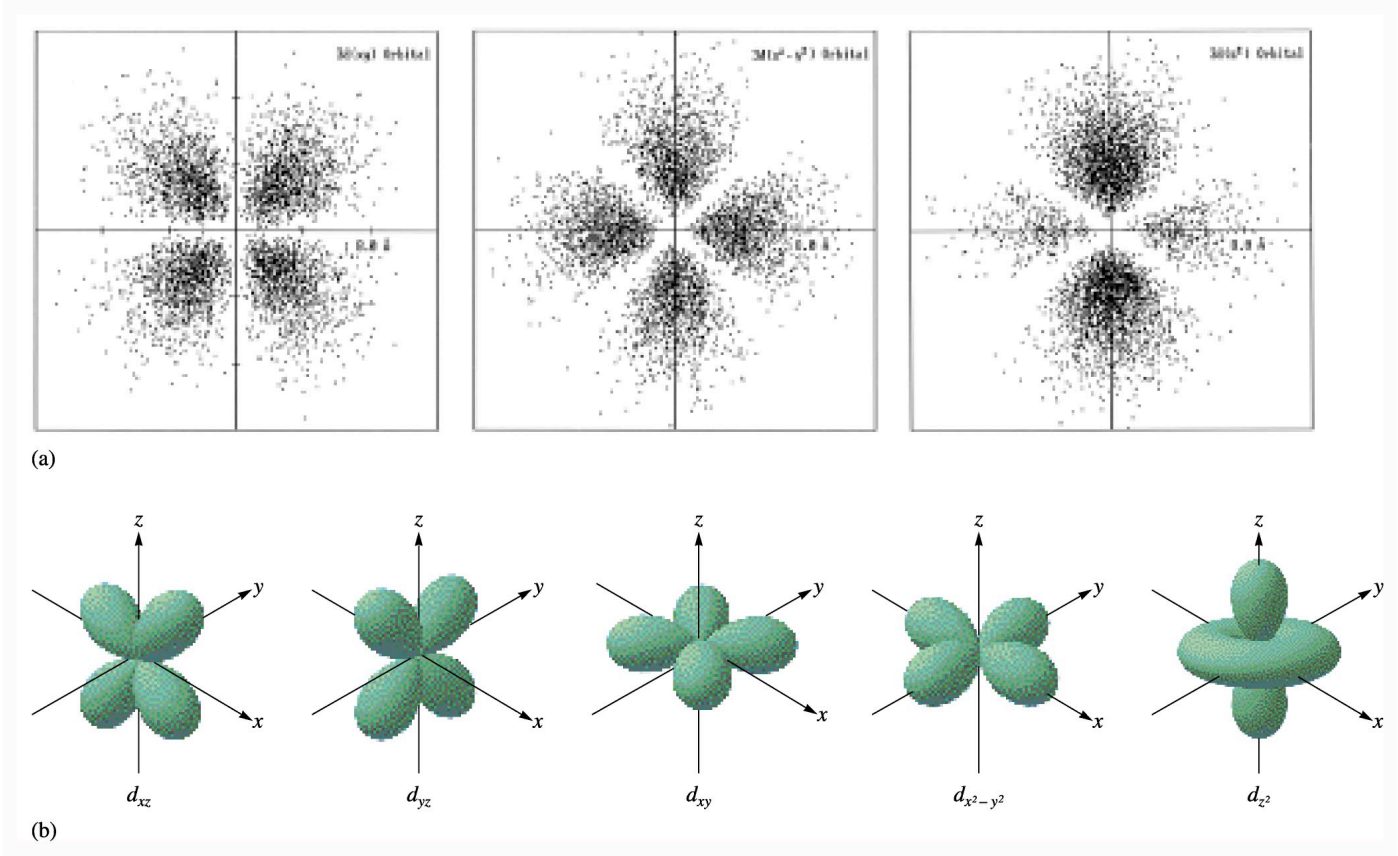
3p orbitals

$$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2}\left(6\sigma - \sigma^2\right)e^{-\sigma/3}\cos\theta$$

- more nodes as compared to 2p (expected.).
- still can be represented by a “dumbbell” contour.

Orbital Shapes (cont.)

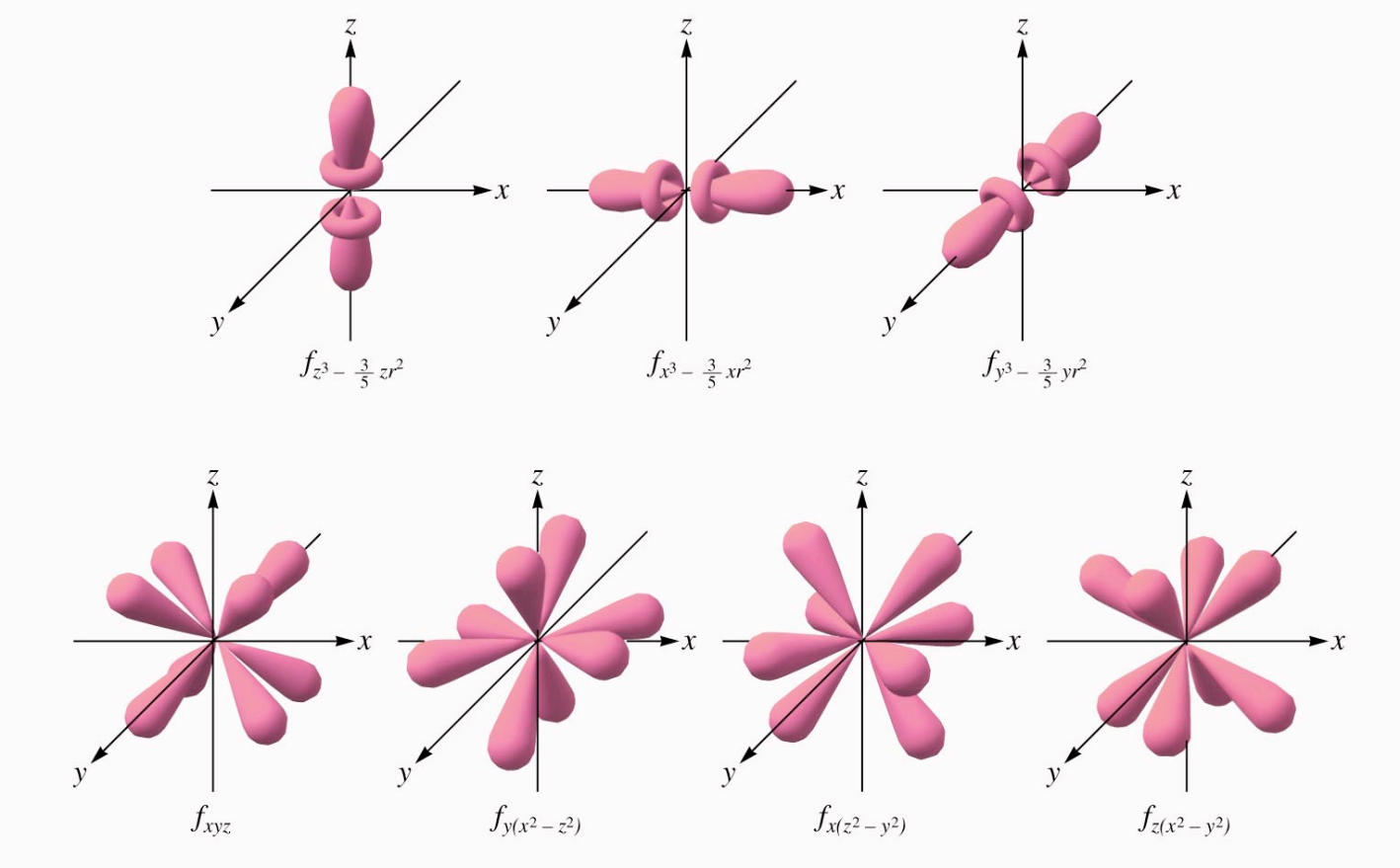
3d (l = 2) orbitals



- **labeled as d_{xz}, d_{yz}, d_{xy}, d_{x2-y2} and d_{z2}.**

Orbital Shapes (cont.)

4f (l = 3) orbitals



- exceedingly complex probability distributions.