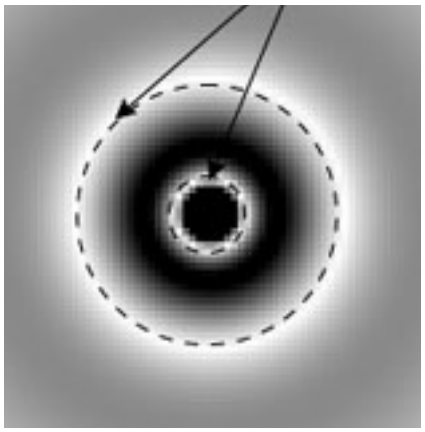


PH575 Spring 2019

Review Lecture #1a

Complex numbers

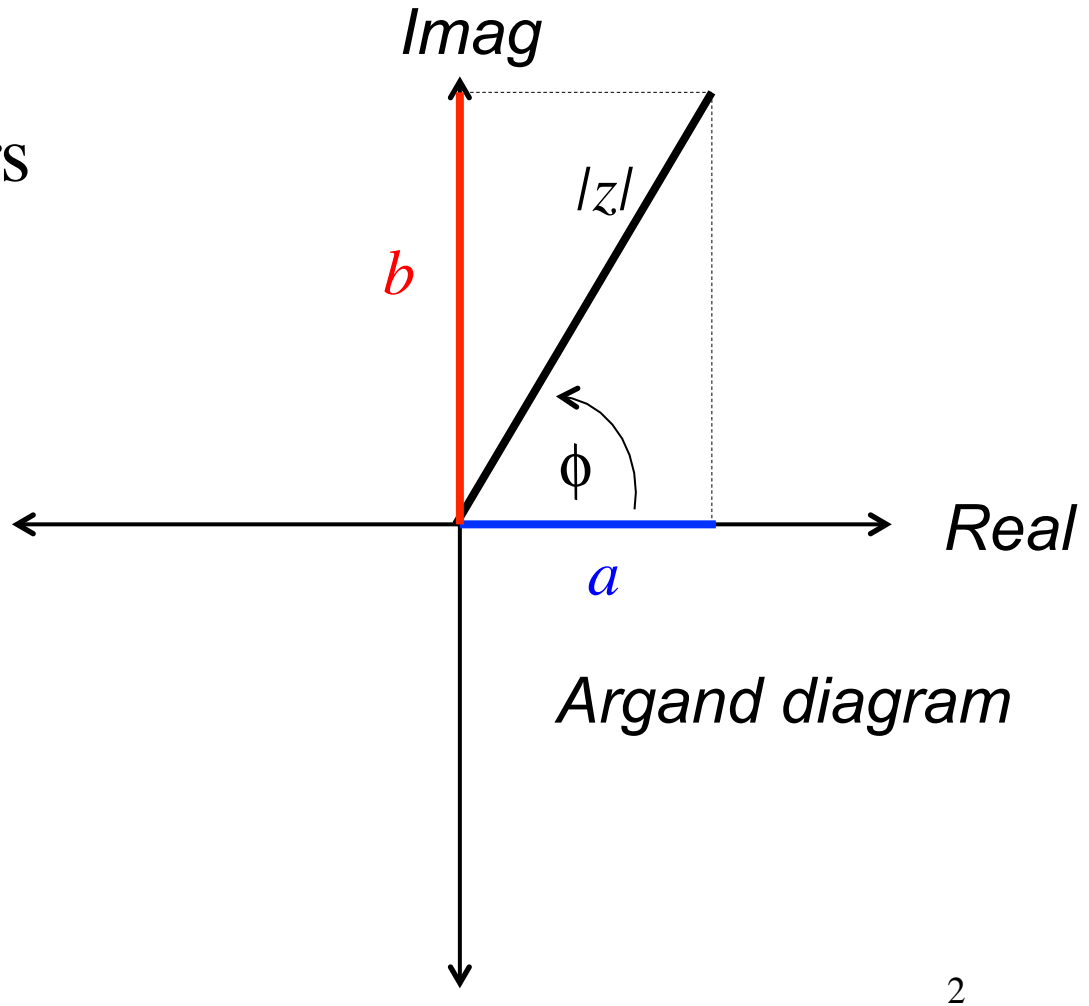
April 1, 2019

Complex numbers

$$i = \sqrt{-1}$$

$$z = a + ib \qquad z = |z|e^{i\phi}$$

$$\left.\begin{aligned} \mathrm{Re}(z) &= a \\ \mathrm{Im}(z) &= b \end{aligned}\right\} \text{real numbers}$$



$$|z| = \sqrt{a^2 + b^2}$$

$$\tan\phi = \frac{b}{a}$$

Euler's relation

$$\exp(i\phi) = \cos\phi + i\sin\phi$$

Consistency argument

$$z = a + ib \qquad\qquad z = |z|e^{i\phi}$$

If these represent the same thing, then the assumed Euler relationship says:

$$a + ib = |z|\cos\phi + i|z|\sin\phi$$

Equate real parts: $a = |z|\cos\phi$

Equate imaginary parts: $b = |z|\sin\phi$

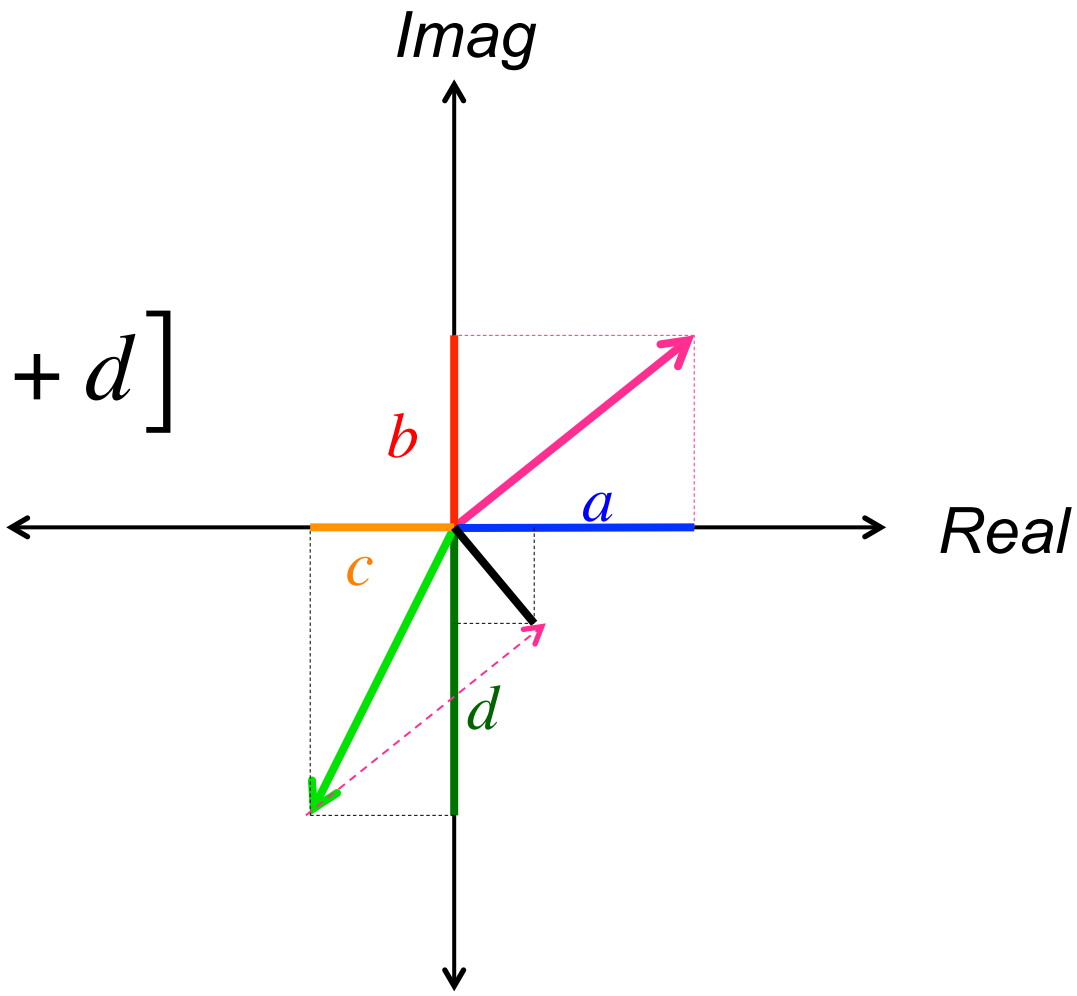
$$|z| = \sqrt{a^2 + b^2}$$

$$\tan\phi = \frac{b}{a}$$

Adding complex numbers is easy in rectangular form

$$z = a + ib$$
$$w = c + id$$

$$z + w = \left[a + c\right] + i\left[b + d\right]$$

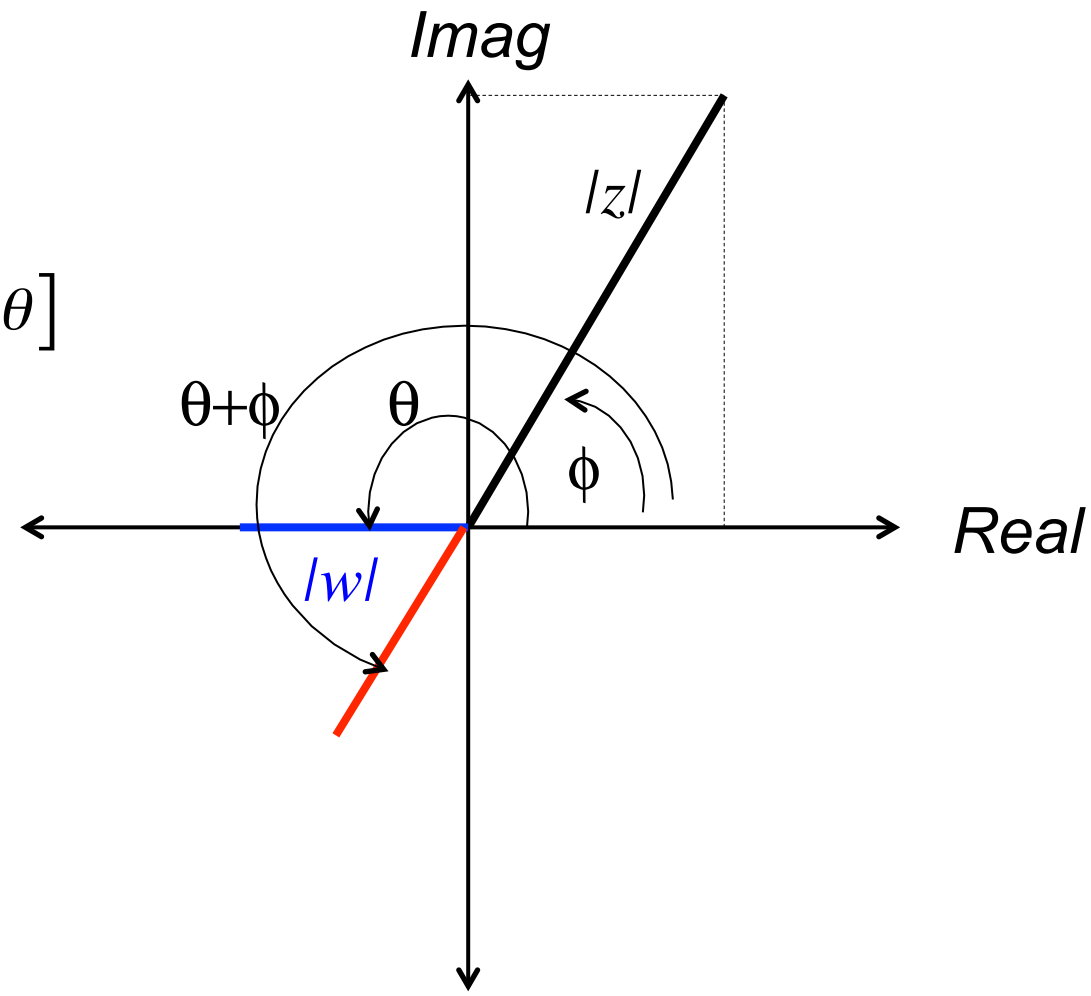


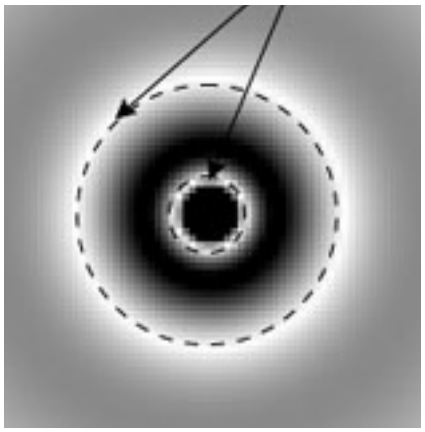
Multiplication and division of complex numbers is easy in *polar* form

$$z = |z| e^{i\phi}$$

$$w = |w| e^{i\theta}$$

$$zw = |z||w| e^{i[\phi+\theta]}$$





PH575 Spring 2019

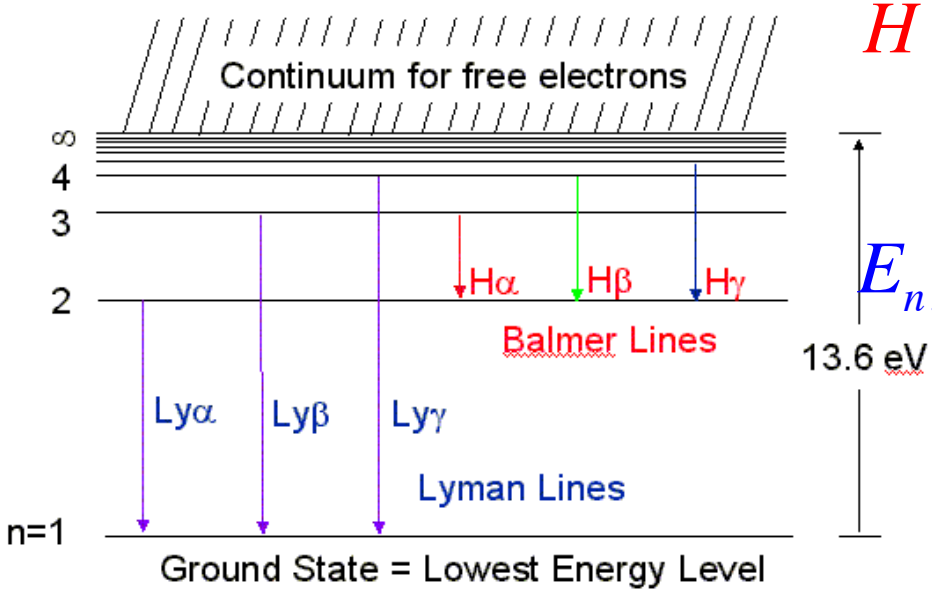
Review Lecture #1b

Atomic orbitals, quantum numbers

April 1, 2019

Atomic states (Hydrogen Atom; wave function form)

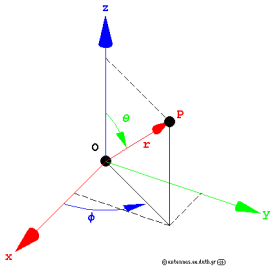
$$\hat{H}R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi) = E_{n,\ell,m_\ell,m_s}R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi)$$



$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$ Hamiltonian

$$E_{n,\ell,m_\ell,m_s} = -\frac{e^2}{2n^2(4\pi\varepsilon_0)a_0} = -\frac{13.6}{n^2}e$$

Energy eigenvalues => spectrum



$$R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi)\chi_{m_s}$$ Eigenfunctions; wave functions

$$\left|R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi)\chi_{m_s}\right|^2$$ => electron distribution

Visualize electron clouds

https://winter.group.shef.ac.uk/orbitron/

Explore
Compare s (or p, d) orbitals for different n
Compare s,p,d etc within given n
Explore tabs – electron density, equations
Energy
Hybrids (linear combinations)

The Hydrogen Atom

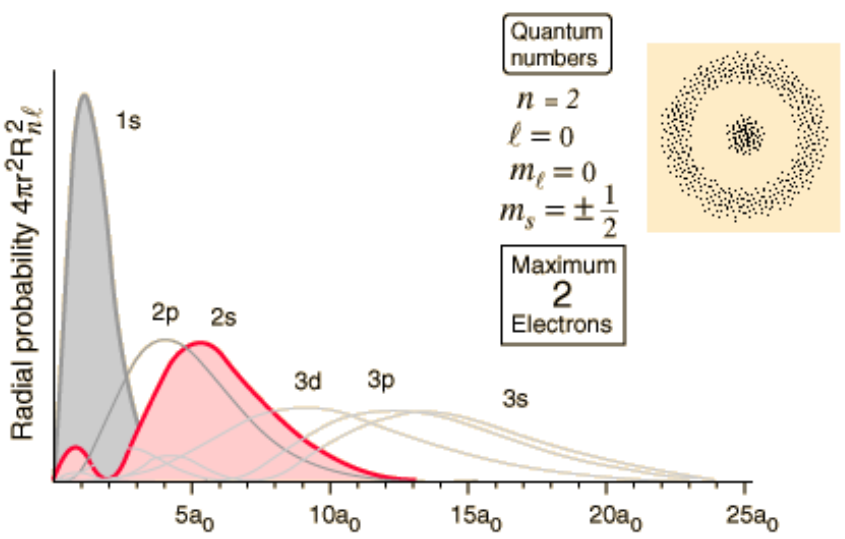
$$\left|\varphi_{n,\ell,m_\ell,m_s}\right\rangle \quad \left\langle \vec{r}\middle|\varphi_{n,\ell,m_\ell,m_s}\right\rangle = R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi)\chi_{m_s}$$

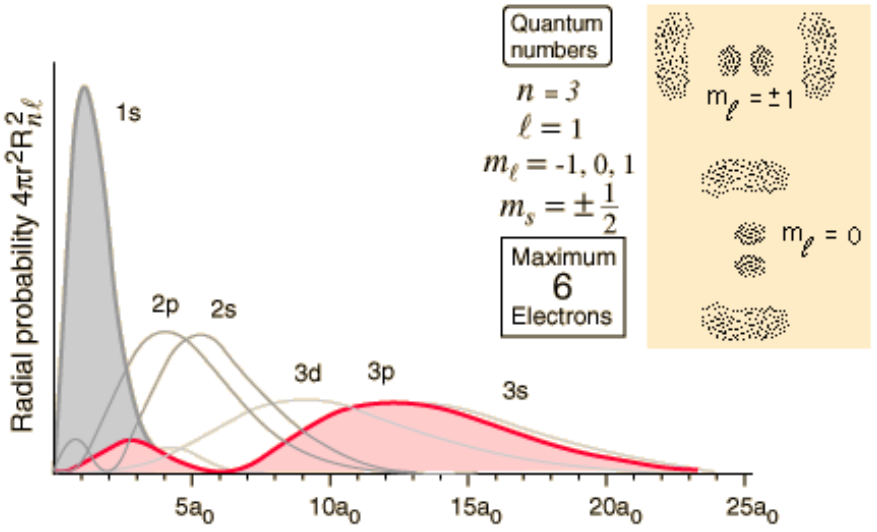
Quantum numbers	
n	Principal quantum number. Sets avg. distance from nucleus. Sets energy scale. n =1,2,3,4 …
l	Orbital angular momentum is $\sqrt{\ell(\ell+1)}\hbar$ l = 0(s), 1(p), 2(d), 3(f), …n-1
m_l	Magnetic quantum number gives orb. am projection on z- axis. m_l = 0, ±1, ±2 … ±l
s	Spin quantum number is always 1/2 for an electron.
m_s	Spin magnetic quantum number gives spin am projection on z-axis. m_s = ±1/2

Atomic states - radial
(Hydrogen Atom; wave function form)

$$\left\langle \vec{r} \middle| \varphi_{n,\ell,m_\ell,m_s} \right\rangle = R_{n,\ell}(r) Y_{\ell,m_\ell}(\theta,\phi) \chi_{m_s}$$

Radial wavefunction - size of electron cloud



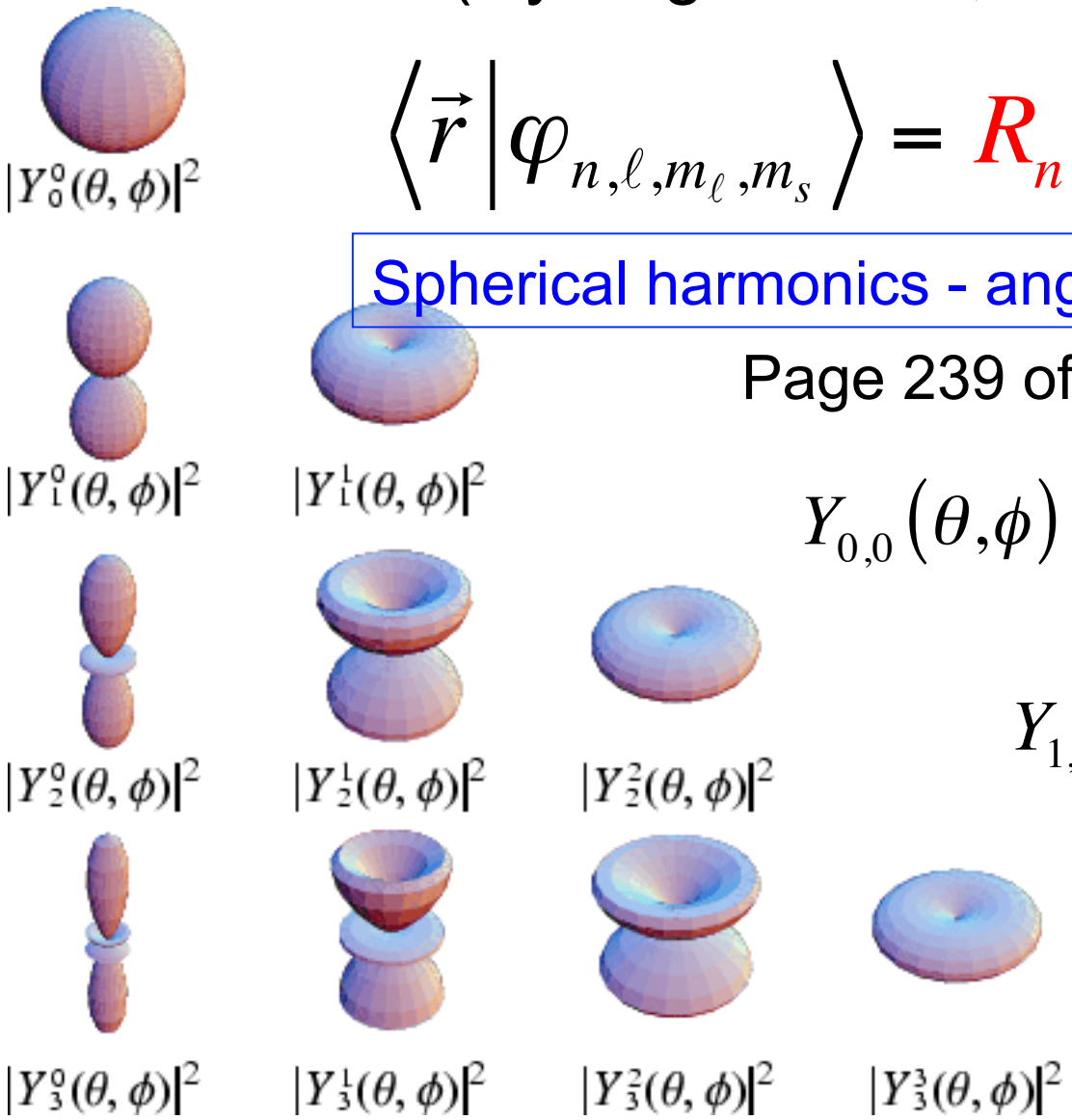


Atomic states – angular; complex
(Hydrogen Atom; wave function form)

$$\left\langle \vec{r} \middle| \varphi_{n,\ell,m_\ell,m_s} \right\rangle = R_{n,\ell}(r) Y_{\ell,m_\ell}(\theta,\phi) \chi_{m_s}$$

Spherical harmonics - angular dependence - bonding

Page 239 of Sutton lists these functions

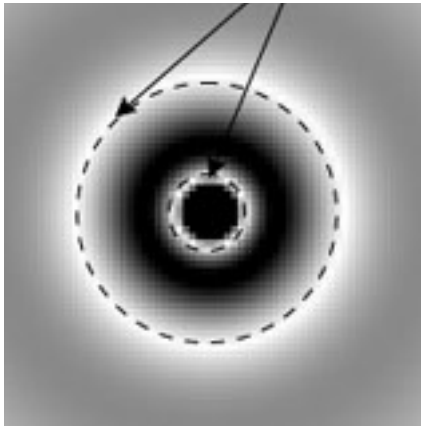


$$Y_{0,0}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$$

Spherically symmetric
$l = 0$

$$Y_{1,\pm1}(\theta,\phi) = \mp\frac{3}{\sqrt{8\pi}}\sin\theta\, e^{\pm i\phi}$$

$$\left|Y_\ell^{m_\ell}(\theta,\phi)\right|^2$$



$$\langle n\ell m_\ell | n\ell m_\ell \rangle$$

$$\sum_i |i\rangle\langle i| = 1$$

$$\beta = \langle 1 | \hat{H} | 2 \rangle$$

PH575 Spring 2019

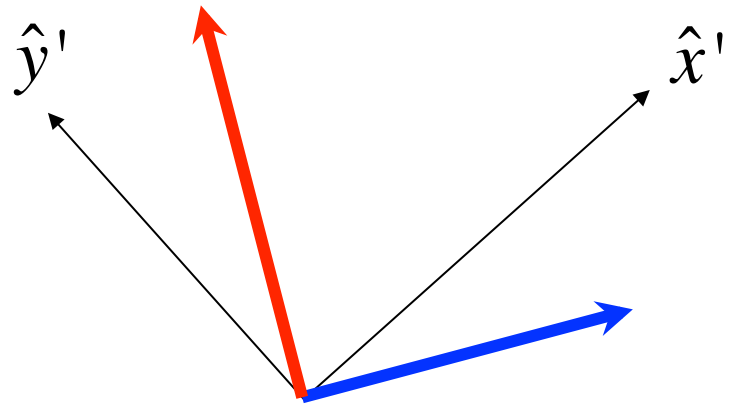
Lecture #1 -
Review of atomic wave functions
Review of bra-ket notation and quantum mechanics concepts

Sutton Ch. 2 pp 21-25
(McIntyre Ch 1-3)

H atom atomic orbitals form an orthonormal set

Two **vectors** are orthogonal if

$$\vec{a} \bullet \vec{b} = a_1 b_1 + a_2 b_2 + a_3 b_3 + \ldots = 0$$



A **vector** is normalized if

$$\vec{a} \bullet \vec{a} = a_1 b_1 + a_2 a_2 + a_3 a_3 + \ldots = 1$$

H atom atomic orbitals form an orthonormal set

A **function** is a giant, dense, vector. *e.g.*

$$f = (...4,1,0,1,4,9...)$$

Define "dot product" or "projection" of 2 functions:

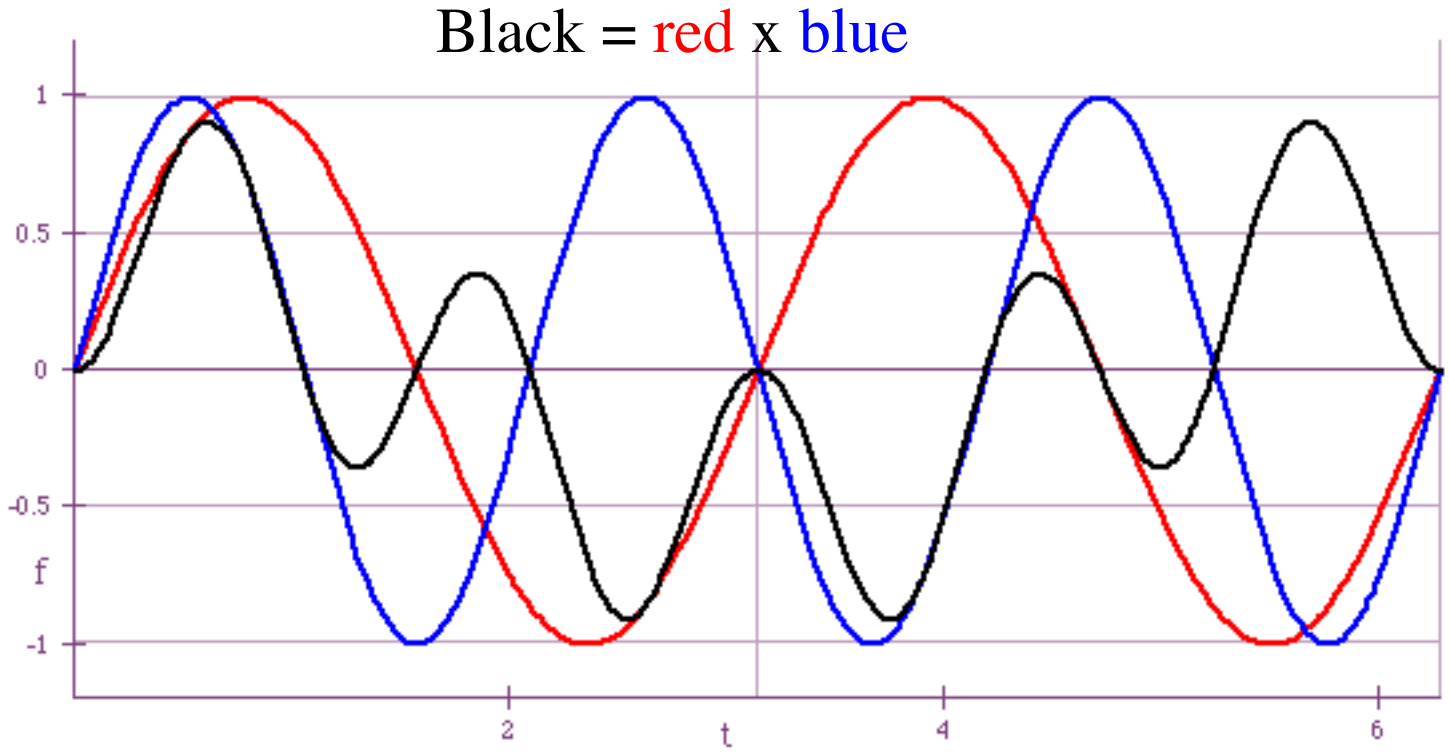
$$"f(x) \bullet g(x)" = \sum_{x_i} f^*(x_i) g(x_i)$$

$$\rightarrow \int_{all\ space} f^*(x) g(x) dx$$

Two **functions** are orthogonal if $\int_{all\ space} f^*(x) g(x) dx = 0$

A **function** is normalized if $\int_{all\ space} f^*(x) f(x) dx = 1$

The red function is sin(*kx*). The blue function is sin(2*kx*). The black function is sin(*kx*) * sin(2*kx).*



- "All of space" is two cycles of the red function.
- The integral of the black function over all space is …..
- Zero! The projection of sin(*kx*) onto sin(2*kx*) is zero

H atom atomic orbitals form an orthonormal set

H atomic **functions**:

$$\iiint_{allspace} R^{*}_{n',\ell'}(r)\,Y^{*}_{\ell',m_{\ell}'}(\theta,\phi)\,R_{n,\ell}(r)\,Y_{\ell,m_{\ell}}(\theta,\phi)\,dV = \delta_{nn'}\delta_{\ell\ell'}\delta_{m_{\ell}m_{\ell}'}$$

Angular and radial parts are also separately orthonormal:

$$\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} Y^{*}_{\ell',m_{\ell}'}(\theta,\phi)\,Y_{\ell,m_{\ell}}(\theta,\phi)\underbrace{\sin\theta\,d\theta\,d\phi}_{d\Omega} = \delta_{\ell\ell'}\delta_{m_{\ell}m_{\ell}'}$$

Now use “bra-ket” notation for the same thing ….

H atom atomic orbitals form an orthonormal set

Now use "bra-ket" notation for the same thing ….

$$\left\langle \ell', m_\ell' \middle| \ell, m_\ell \right\rangle \equiv \int_{all} Y^*_{\ell', m_\ell'}(\theta,\phi) Y_{\ell, m_\ell}(\theta,\phi) d\Omega$$

$$= \delta_{\ell\ell'} \delta_{m_\ell m_\ell'}$$

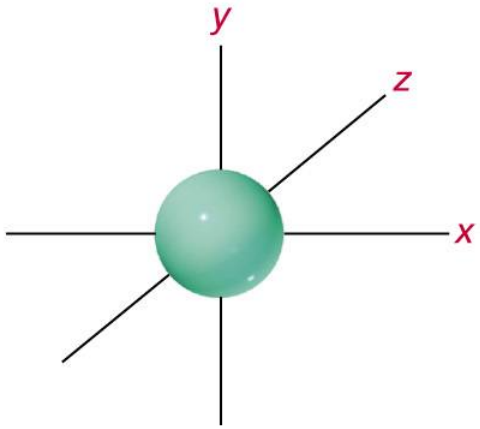
Ket: $\left| \ell, m_\ell \right\rangle \doteq Y_{\ell, m_\ell}(\theta,\phi)$

Bra = complex conjugate of ket: $\left\langle \ell, m_\ell \right| \doteq Y^*_{\ell, m_\ell}(\theta,\phi)$

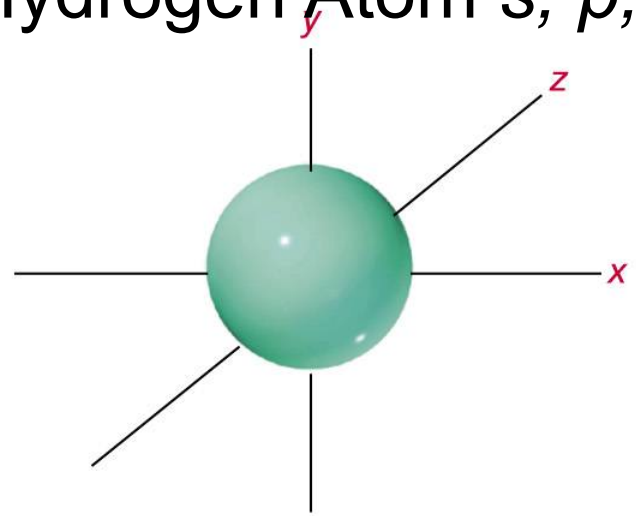
$\langle \ | \ \rangle$ = integrate over all space

$\doteq$ "dot equals" means "is represented by"

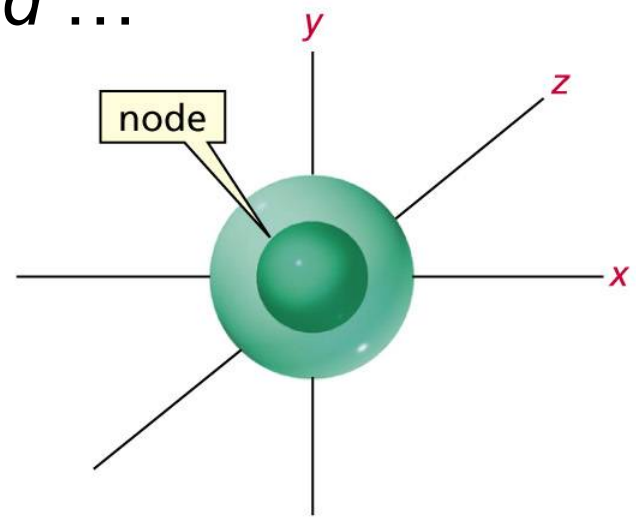
The Hydrogen Atom *s*, *p*, *d* …



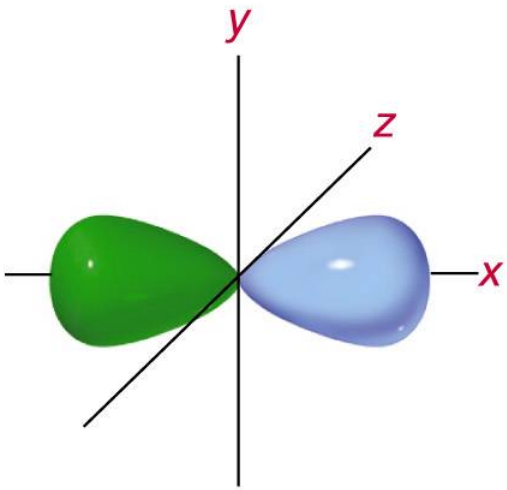
1*s* atomic orbital



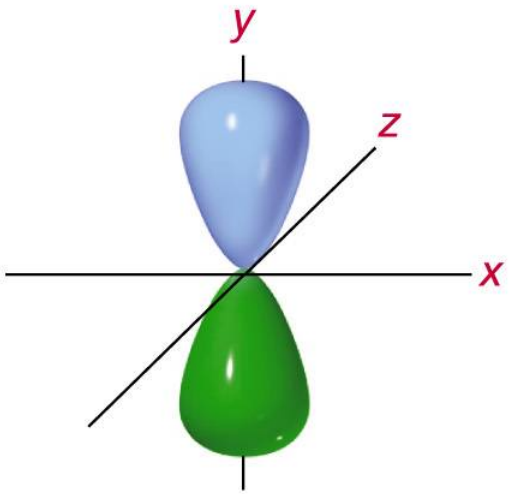
2*s* atomic orbital
node not shown



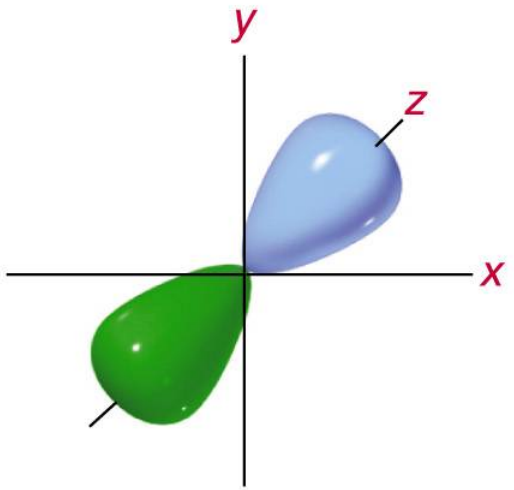
2*s* atomic orbital
node shown



$2p_x$ orbital

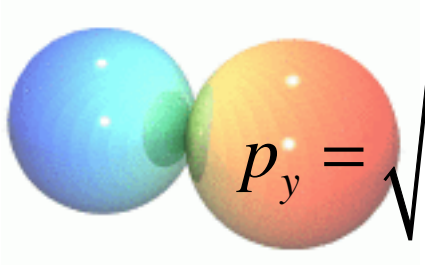


$2p_y$ orbital



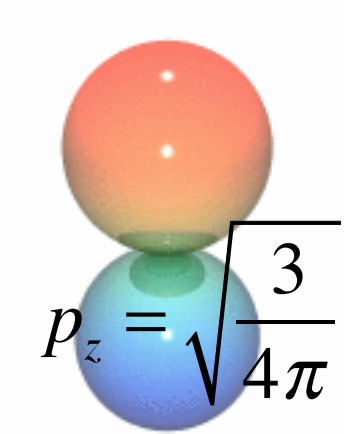
$2p_z$ orbital

The Hydrogen Atom *s*, *p*, *d* …

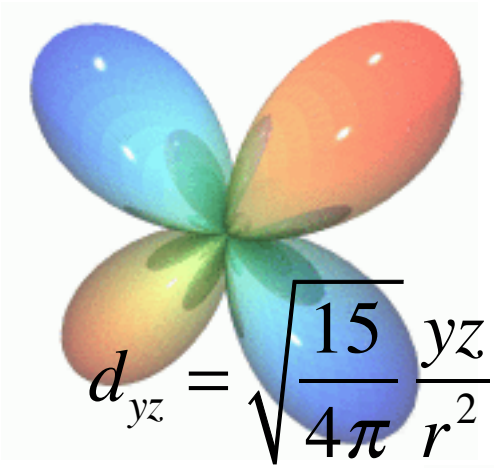


$$p_y = \sqrt{\frac{3}{4\pi}}\frac{y}{r}$$

$$\langle \vec{r} | p_x \rangle = \sqrt{\frac{3}{4\pi}} R_{n,1}(r)\frac{x}{r}$$

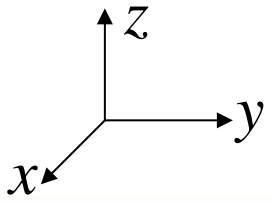


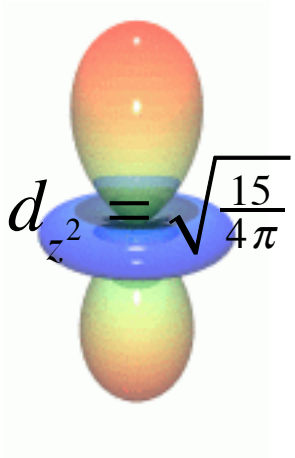
$$p_z = \sqrt{\frac{3}{4\pi}}\frac{z}{r}$$



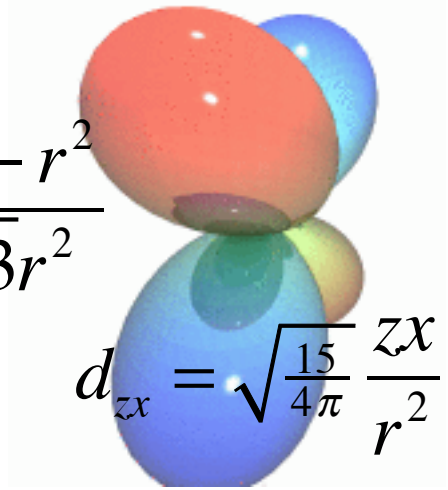
$$d_{yz} = \sqrt{\frac{15}{4\pi}}\frac{yz}{r^2}$$

s, *p*, *d etc.* orbitals are linear combinations of spherical harmonics that are real & often more convenient. (Sutton 1.21, 1.22)

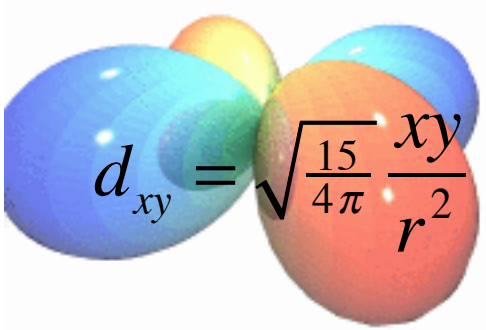




$$d_{z^2} = \sqrt{\frac{15}{4\pi}}\frac{3z^2 - r^2}{2\sqrt{3}r^2}$$



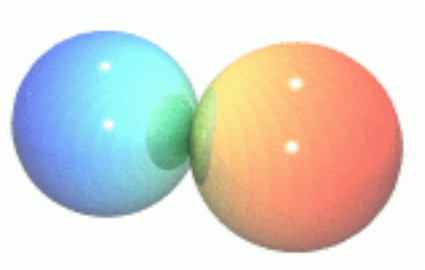
$$d_{zx} = \sqrt{\frac{15}{4\pi}}\frac{zx}{r^2}$$



$$d_{xy} = \sqrt{\frac{15}{4\pi}}\frac{xy}{r^2}$$

$$d_{x^2-y^2} = \sqrt{\frac{15}{4\pi}}\frac{x^2 - y^2}{2r^2}$$

p orbitals are linear combinations of Y_{1m}



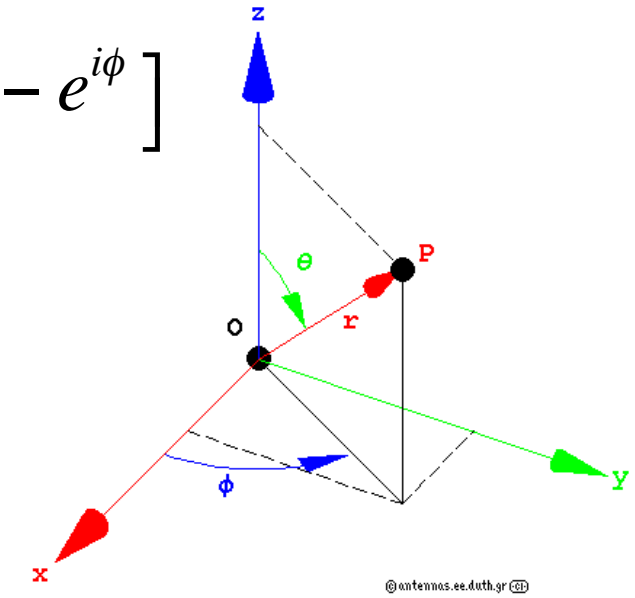
$$p_y = \sqrt{\frac{3}{4\pi}}\frac{y}{r}$$

p_y is a linear combination of the $Y_{1,1}$ and $Y_{1,-1}$ spherical harmonics.

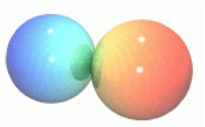
$$\frac{i}{\sqrt{2}}\left[Y_{1,-1} + Y_{1,1}\right] = \frac{i}{\sqrt{2}}\sqrt{\frac{3}{8\pi}}\sin\theta\left[e^{-i\phi} - e^{i\phi}\right]$$

$$\frac{-2ii}{\sqrt{2}}\sqrt{\frac{3}{8\pi}}\sin\theta\sin\phi = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$$

$$= \sqrt{\frac{3}{4\pi}}\frac{y}{r} = p_y$$



Deconstruct *p* orbitals into Y_{1m} components by projecting




$$\left|p_y\right\rangle = \left\langle Y_{1,-1}\middle|p_y\right\rangle \left|Y_{1,-1}\right\rangle + \left\langle Y_{1,+1}\middle|p_y\right\rangle \left|Y_{1,+1}\right\rangle + \left\langle Y_{1,0}\middle|p_y\right\rangle \left|Y_{1,0}\right\rangle$$

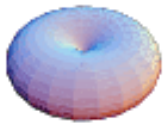
Projection of $\left|p_y\right\rangle$ on $\left|Y_{1,-1}\right\rangle$ | Projection of $\left|p_y\right\rangle$ on $\left|Y_{1,+1}\right\rangle$ | Projection of $\left|p_y\right\rangle$ on $\left|Y_{1,0}\right\rangle$

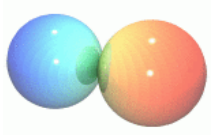
Project p_y onto $Y_{1\text{-}1}$:

$$\left\langle Y_{1,-1}\middle|p_y\right\rangle = ?$$

Deconstruct *p* orbitals into Y_{1m} components by projecting

$$\left\langle Y_{1,-1} \middle| p_y \right\rangle = \left\langle \; \right| \; \left. \right\rangle = \int_{volume} Y_{1,-1}^{*} p_y \, d\Omega$$





$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} \left(\frac{3}{4\pi}\right)^{1/2} \frac{y}{r} \sin\theta d\theta d\phi$$

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} \left(\frac{3}{4\pi}\right)^{1/2} \frac{r\sin\theta\sin\phi}{r} \sin\theta d\theta d\phi$$

$$\frac{1}{\sqrt{2}}\left(\frac{3}{4\pi}\right) \underbrace{\int_{\theta=0}^{\pi} \sin^3\theta d\theta}_{4/3} \underbrace{\int_{\phi=0}^{2\pi} \sin\phi e^{i\phi} d\phi}_{i\pi} = \frac{i}{\sqrt{2}}$$

Expect this!

Language: The ket $|p_y\rangle$ is a *superposition* of the kets $|Y_{1,m}\rangle$, and the numbers $\langle Y_{1,m_\ell}|p_y\rangle$ are the projections of $|p_y\rangle$ onto the basis kets.

$$|p_y\rangle = \langle Y_{1,-1}|p_y\rangle |Y_{1,-1}\rangle + \langle Y_{1,+1}|p_y\rangle |Y_{1,+1}\rangle + \langle Y_{1,0}|p_y\rangle |Y_{1,0}\rangle$$

$$\langle Y_{1,-1}|p_y\rangle = \frac{i}{\sqrt{2}}; \langle Y_{1,+1}|p_y\rangle = \frac{i}{\sqrt{2}}; \langle Y_{1,0}|p_y\rangle = 0$$

The same thing is stated more generally in Sutton 2.2

$$|\Psi\rangle = \sum_{all\ |\phi\rangle} |\phi\rangle\langle\phi|\Psi\rangle$$

Backup slides on projections of functions

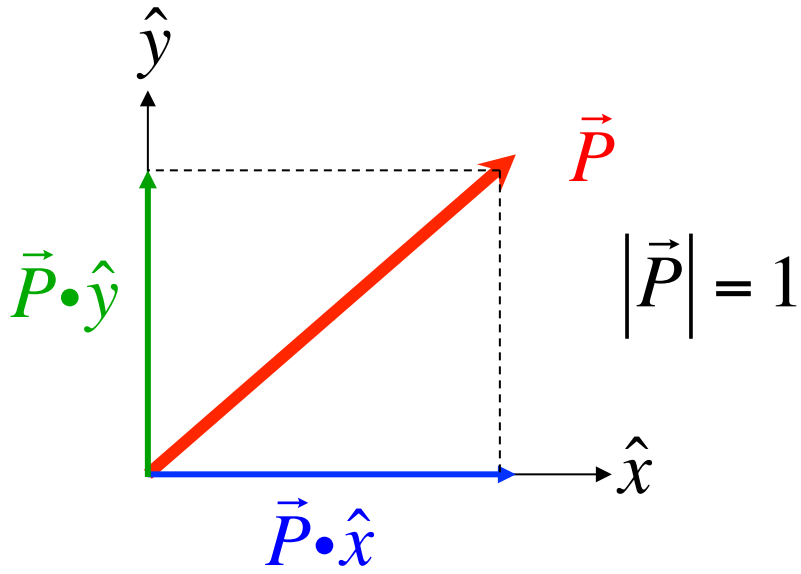
This is a vector, $\vec{P}$ represented in one coordinate system

$$\vec{P} = \vec{P}\bullet\hat{x}\,\hat{x} + \vec{P}\bullet\hat{y}\,\hat{y}$$

Projection of $\vec{P}$ on $\hat{x}$ Projection of $\vec{P}$ on $\hat{y}$

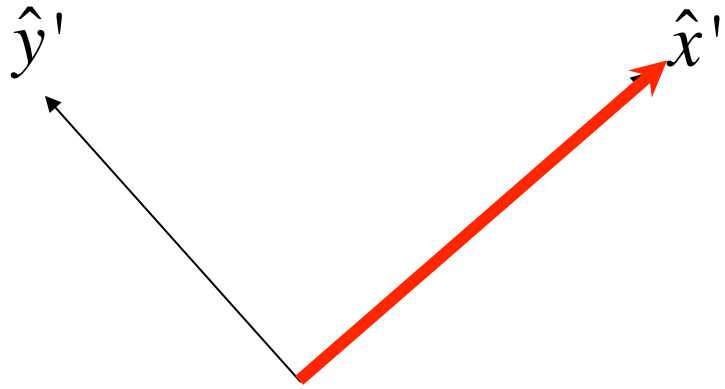
$$\vec{P} = \frac{1}{\sqrt{2}}\hat{x} + \frac{1}{\sqrt{2}}\hat{y}$$

(Sutton Eq. 2.1)



This is the SAME vector, $\vec{P}$ represented in another coordinate system

$$\vec{P} = 1\,\hat{x}' + 0\,\hat{y}'$$



A ket, $|\varphi\rangle$, is similar to a vector: we represent it by "projecting" it onto "basis kets" (similar to the axes of the coordinate system)

$$|p_y\rangle = \langle Y_{1,-1}|p_y\rangle |Y_{1,-1}\rangle + \langle Y_{1,+1}|p_y\rangle |Y_{1,+1}\rangle + \langle Y_{1,0}|p_y\rangle |Y_{1,0}\rangle$$

Projection of $|p_y\rangle$ on $|Y_{1,-1}\rangle$ Projection of $|p_y\rangle$ on $|Y_{1,+1}\rangle$ Projection of $|p_y\rangle$ on $|Y_{1,0}\rangle$

A bra, $\langle\varphi|$, is the complex conjugate of a ket.
A "bra-ket" is simply a projection of one "state" on another. Also called an *overlap integral*.

$$\langle\psi|\phi\rangle = \int_{volume} \psi(\vec{r})^* \phi(\vec{r}) dV$$

We understand what it means to "project" one vector onto another …

$$\vec{P} = \left(P_x \, , P_y \right) \qquad \vec{Q} = \left(Q_x \, , Q_y \right)$$

$$\vec{P} \cdot \vec{Q} = P_x Q_x + P_y Q_y$$

- Multiply components and add the products.

So what does it mean to "project" one function onto another?

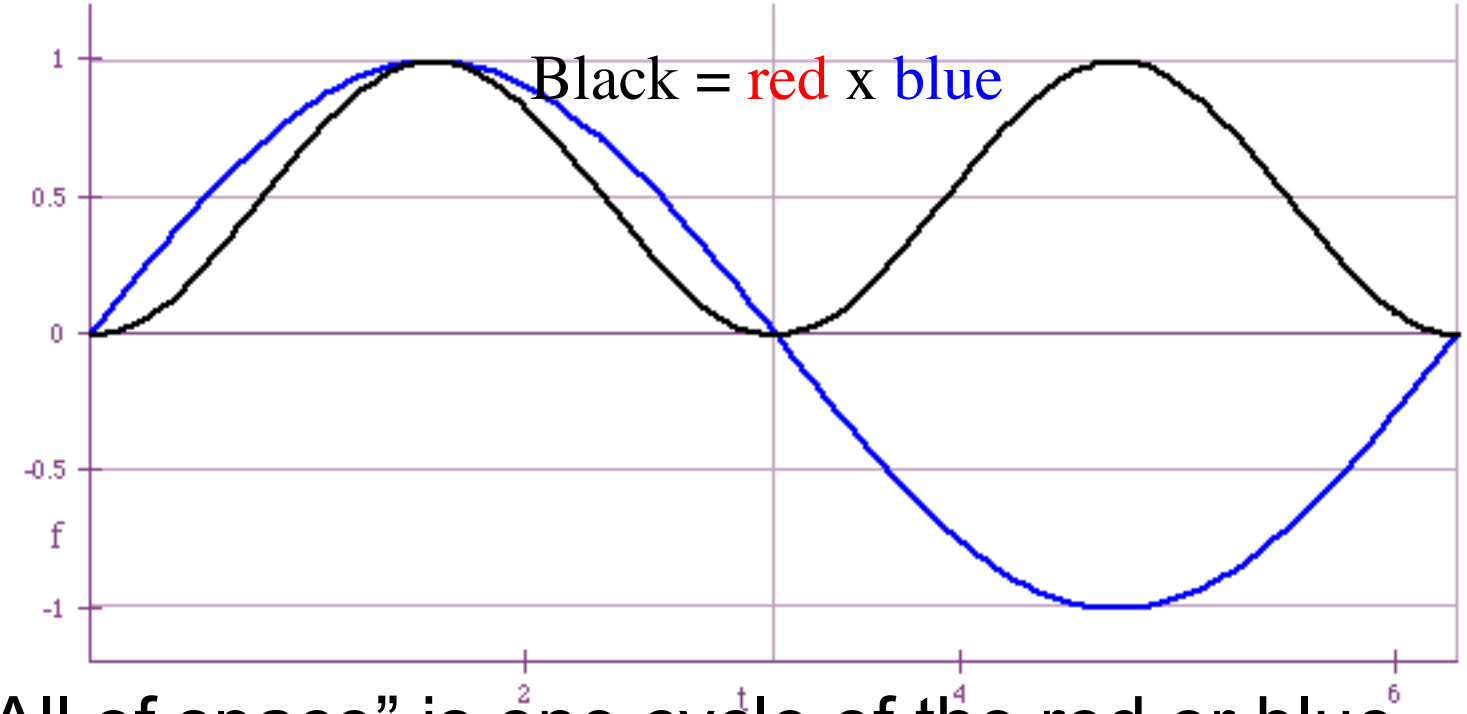
Think of a function as a vector with *many* components - each component is the value of the function at a particular point in space:

- At every point in space, multiply the values of the two functions together.
- Add these products. (But now "adding" means "integrating")
- The resulting number is the projection of one function onto the other.

$$\left\langle \phi_i \middle| \phi_j \right\rangle = \int_{space} \phi_i^*(\vec{r})\phi_j(\vec{r})dV$$

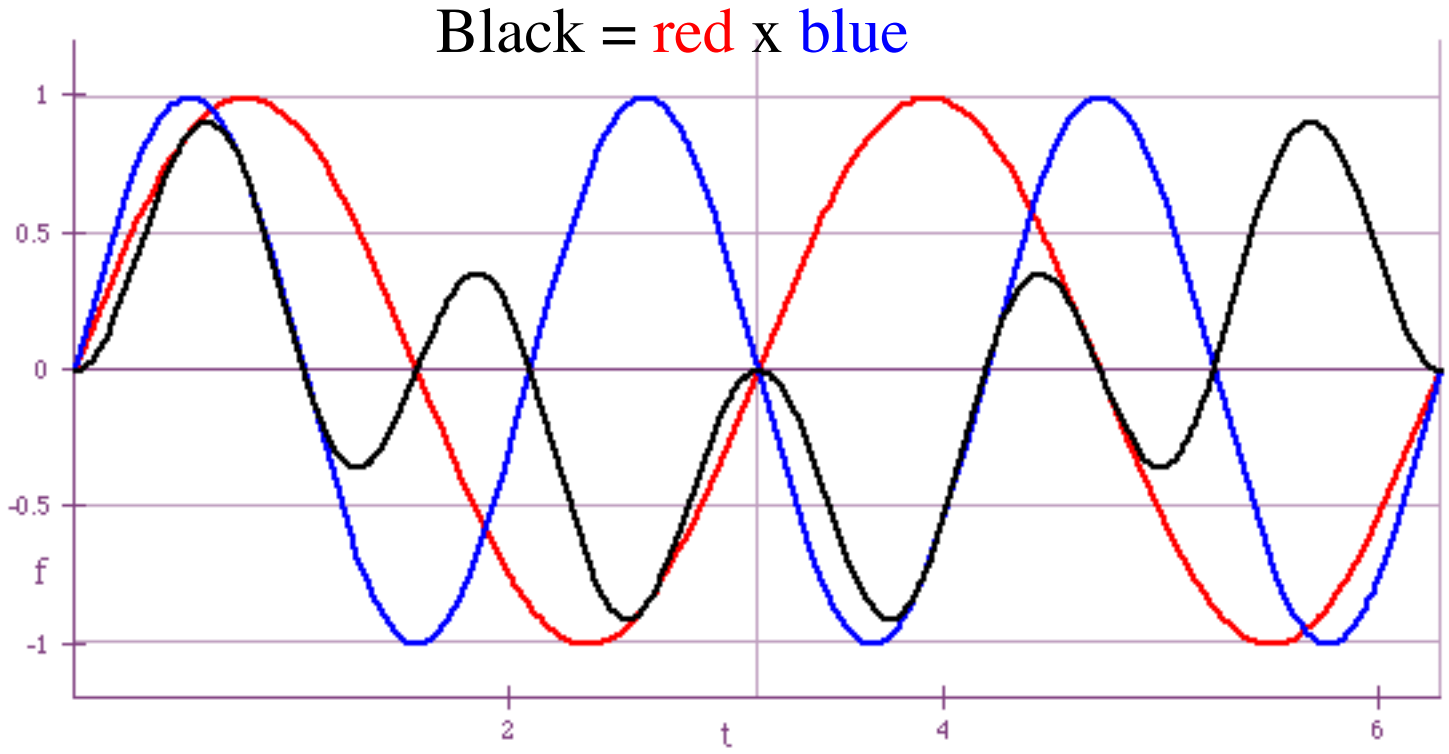
Here are some examples …

The blue function is sin(*kx*). The red function is also sin(*kx*) – it's under the blue one. The black function is $\sin^2(kx)$ - the product of the two.



- "All of space" is one cycle of the red or blue function.
- The integral of the black function over all space is …..
- Not zero! The projection of sin(*kx*) onto itself is 1!

The red function is sin(*kx*). The blue function is sin(2*kx*). The black function is sin(*kx*) * sin(2*kx).*



- "All of space" is two cycles of the red function.
- The integral of the black function over all space is …..
- Zero! The projection of sin(*kx*) onto sin(2*kx*) is zero

If the projection of one function onto another is zero, we say the functions are orthogonal.

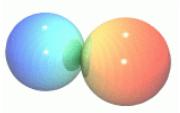
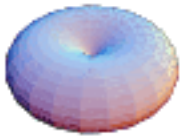
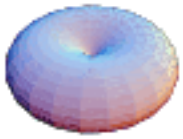
The projection of a function onto itself is always a positive definite number, which we can arrange to be unity by appropriate choice of normalizing constant.

If a set of functions f_i form an orthonormal set, then we can say that

$$\left\langle \phi_i \middle| \phi_j \right\rangle = \int_{space} \phi_i^*(\vec{r})\phi_j(\vec{r})dV = \delta_{ij}$$

where the Kronecker delta $\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$

An example with H-atom wave functions


$$\left|p_y\right\rangle = \left\langle Y_{1,-1}\middle|p_y\right\rangle \left|Y_{1,-1}\right\rangle + \left\langle Y_{1,+1}\middle|p_y\right\rangle \left|Y_{1,+1}\right\rangle + \left\langle Y_{1,0}\middle|p_y\right\rangle \left|Y_{1,0}\right\rangle$$

Projection of $\left|p_y\right\rangle$ on $\left|Y_{1,-1}\right\rangle$

Projection of $\left|p_y\right\rangle$ on $\left|Y_{1,+1}\right\rangle$

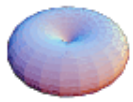
Projection of $\left|p_y\right\rangle$ on $\left|Y_{1,0}\right\rangle$

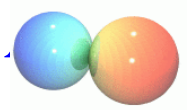
Last time we saw that $\left|p_y\right\rangle = \frac{i}{\sqrt{2}}\left[\left|Y_{1,-1}\right\rangle + \left|Y_{1,1}\right\rangle\right]$

$$\left\langle Y_{1,-1}\middle|p_y\right\rangle = \frac{i}{\sqrt{2}} \qquad \left\langle Y_{1,+1}\middle|p_y\right\rangle = \frac{i}{\sqrt{2}} \qquad \left\langle Y_{1,0}\middle|p_y\right\rangle = 0$$

EXAMPLE: Projection of p_y orbital onto spherical harmonic with l = 1, m_l = -1

$$\left\langle Y_{1,-1} \middle| p_y \right\rangle = \left\langle \; \right| \; \left. \right\rangle = \int_{volume} Y_{1,-1}^{*} p_y dV$$





$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} \left(\frac{3}{4\pi}\right)^{1/2} \frac{y}{r} \sin\theta d\theta d\phi$$

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi} \left(\frac{3}{4\pi}\right)^{1/2} \frac{r\sin\theta\sin\phi}{r} \sin\theta d\theta d\phi$$

$$\frac{1}{\sqrt{2}}\left(\frac{3}{4\pi}\right) \underbrace{\int_{\theta=0}^{\pi} \sin^3\theta d\theta}_{4/3} \underbrace{\int_{\phi=0}^{2\pi} \sin\phi e^{i\phi} d\phi}_{i\pi} = \frac{i}{\sqrt{2}}$$

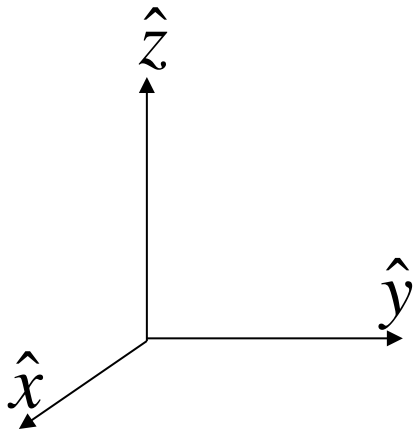
Language: The ket $|p_y\rangle$ is a *superposition* of the kets $|Y_{1,m}\rangle$, and the numbers $\langle Y_{1,m_\ell}|p_y\rangle$ are the projections of $|p_y\rangle$ onto the basis kets.

$$|p_y\rangle = \langle Y_{1,-1}|p_y\rangle |Y_{1,-1}\rangle + \langle Y_{1,+1}|p_y\rangle |Y_{1,+1}\rangle + \langle Y_{1,0}|p_y\rangle |Y_{1,0}\rangle$$

The same thing is stated more generally in Sutton 2.2

$$|\Psi\rangle = \sum_{all\ |\phi\rangle} |\phi\rangle\langle\phi|\Psi\rangle$$

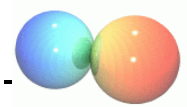
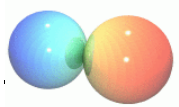
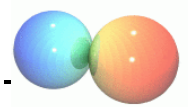
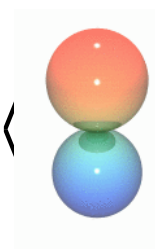
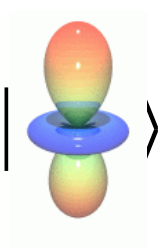
The axes of the coordinate system are *orthonormal*.



$$\hat{x}\cdot\hat{y} = \hat{y}\cdot\hat{z} = \hat{z}\cdot\hat{x} = 0$$
$$\hat{x}\cdot\hat{x} = \hat{y}\cdot\hat{y} = \hat{z}\cdot\hat{z} = 1$$

The basis kets are also *orthonormal*.

$$\left\langle Y_{\ell,m} \middle| Y_{\ell',m'} \right\rangle = \begin{cases} 1 & \text{if } \ell = \ell' \text{ and } m_\ell = m_\ell' \\ 0 & \text{if } \ell \neq \ell' \text{ or } m_\ell \neq m_\ell' \end{cases}$$

$\langle$  $|$  $\rangle = 1$ $\quad \langle$  $|$  $\rangle = 0$ $\quad \langle$  $|$  $\rangle = 0$

Projections are also called *overlap integrals*.

- Any basis ket of an orthonormal set has no overlap integral with any other, and unit overlap with itself.
- How do we know which kets are suitable basis kets? Any set of functions that are the eigenfunctions of a particular operator form an appropriate set!
- Example: the $Y_{l,m}$ functions are orthonormal and form suitable basis kets. They are the eigenfunctions of the L^2 operator (part of the H atom Hamiltonian)
- Let's prove that the p_x p_y and p_z functions (kets) are an orthonormal set, knowing that the $Y_{l,m}$ functions are an orthonormal set.

The following are true. You'll show something similar about *d* orbitals and $Y_{2,m}$ for homework

$$\left|p_y\right\rangle = \frac{i}{\sqrt{2}}\left[\left|Y_{1,-1}\right\rangle + \left|Y_{1,1}\right\rangle\right]$$

$$\left|p_x\right\rangle = \frac{1}{\sqrt{2}}\left[\left|Y_{1,-1}\right\rangle - \left|Y_{1,1}\right\rangle\right]$$

$$\left|p_z\right\rangle = \left|Y_{1,0}\right\rangle$$

Now, what is the projection of the p_y ket onto the p_z? $\left\langle p_z \middle| p_y \right\rangle$

$$\left\langle p_z \middle| p_y \right\rangle = \frac{i}{\sqrt{2}}\left\langle p_z \middle|\left[\left|Y_{1,-1}\right\rangle + \left|Y_{1,1}\right\rangle\right]\right.$$

$$\left\langle p_z \middle| p_y \right\rangle = \frac{i}{\sqrt{2}}\left\langle Y_{1,0} \middle|\left[\left|Y_{1,-1}\right\rangle + \left|Y_{1,1}\right\rangle\right]\right.$$

$$\left\langle p_z \middle| p_y \right\rangle = \frac{i}{\sqrt{2}}\left[\underbrace{\left\langle Y_{1,0} \middle| Y_{1,-1}\right\rangle}_{0} + \underbrace{\left\langle Y_{1,0} \middle| Y_{1,+1}\right\rangle}_{0}\right] = 0$$

$$\left|p_z\right\rangle = \left|Y_{1,0}\right\rangle \qquad \left|p_y\right\rangle = \frac{i}{\sqrt{2}}\left[\left|Y_{1,-1}\right\rangle + \left|Y_{1,1}\right\rangle\right]$$

$$\left|p_x\right\rangle = \frac{1}{\sqrt{2}}\left[\left|Y_{1,-1}\right\rangle - \left|Y_{1,1}\right\rangle\right]$$

You show $\left\langle p_x \middle| p_y \right\rangle = 0$

END OF
Backup slides on projections of functions

Spherical Harmonic functions
(be careful – sometimes normalization is different in different sources.)

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{11} = -\sqrt{\frac{3}{8\pi}}\, e^{i\phi}\, \sin\theta$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\, \cos\theta$$

$$Y_{22} = \sqrt{\frac{15}{32\pi}}\, e^{2i\phi}\, \sin^2\theta$$

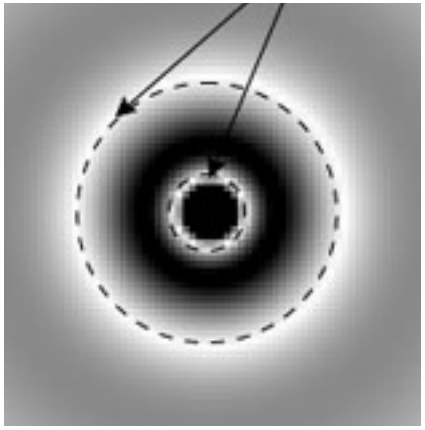
$$Y_{21} = -\sqrt{\frac{15}{8\pi}}\, e^{i\phi}\, \sin\theta\cos\theta$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}}\, (3\cos^2\theta - 1)$$

TABLE 4.1
Angular Factors of Conventional Atomic Orbitals

Symbol	Polar	Cartesian	Normalizing factor
s	1	1	$\frac{1}{2}\left(\frac{1}{\pi}\right)^{1/2}$
p_x	$\sin\theta\cos\phi$	x/r	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}$
p_y	$\sin\theta\sin\phi$	y/r	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}$
p_z	$\cos\theta$	z/r	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}$
d_{z^2}	$(3\cos^2\theta - 1)$	$(3z^2 - r^2)/r^2$ $(2z^2 - x^2 - y^2)/r^2$	$\frac{1}{4}\left(\frac{5}{\pi}\right)^{1/2}$
d_{xz}	$\sin\theta\cos\theta\cos\phi$	xz/r^2	$\frac{1}{2}\left(\frac{15}{\pi}\right)^{1/2}$
d_{yz}	$\sin\theta\cos\theta\sin\phi$	yz/r^2	$\frac{1}{2}\left(\frac{15}{\pi}\right)^{1/2}$

$d_{x^2-y^2}$	$\sin^2\theta\cos 2\phi$	$(x^2-y^2)/r^2$	$\frac{1}{4}\left(\frac{15}{\pi}\right)^{1/2}$
d_{xy}	$\sin^2\theta\sin 2\phi$	xy/r^2	$\frac{1}{4}\left(\frac{15}{\pi}\right)^{1/2}$
f_{z^3}	$(5\cos^3\theta-3\cos\theta)$	$z(5z^2-3r^2)/r^3$ $[2z^3-3z(x^2+y^2)]/r^3$	$\frac{1}{4}\left(\frac{7}{\pi}\right)^{1/2}$
f_{xz^2}	$(5\cos^2\theta-1)\sin\theta\cos\phi$	$x(5z^2-r^2)/r^3$ $[4xz^2-x(x^2+y^2)]/r^3$	$\frac{1}{8}\left(\frac{42}{\pi}\right)^{1/2}$
f_{yz^2}	$(5\cos^2\theta-1)\sin\theta\sin\phi$	$y(5z^2-r^2)/r^3$ $[4yz^2-y(x^2+y^2)]/r^3$	$\frac{1}{8}\left(\frac{42}{\pi}\right)^{1/2}$
f_{xyz}	$\sin^2\theta\cos\theta\sin 2\phi$	xyz/r^3	$\frac{1}{4}\left(\frac{105}{\pi}\right)^{1/2}$
$f_{z(x^2-y^2)}$	$\sin^2\theta\cos\theta\cos 2\phi$	$z(x^2-y^2)/r^3$	$\frac{1}{4}\left(\frac{105}{\pi}\right)^{1/2}$
$f_{x(x^2-3y^2)}$	$\sin^3\theta\cos 3\phi$	$x(x^2-3y^2)/r^3$	$\frac{1}{8}\left(\frac{70}{\pi}\right)^{1/2}$
$f_{y(3x^2-y^2)}$	$\sin^3\theta\sin 3\phi$	$y(3x^2-y^2)/r^3$	$\frac{1}{8}\left(\frac{70}{\pi}\right)^{1/2}$



PH575 Spring 2019

Lecture #1c - Operators
Sutton Ch. 2 pp 21-25
(McIntyre Ch 1-3)

$$\langle n\ell m_\ell | n\ell m_\ell \rangle$$

$$\sum_i |i\rangle\langle i| = 1$$

$$\beta = \langle 1|\hat{H}|2\rangle$$

OPERATORS

are mathematical instructions that represent physical quantities like energy or momentum. They perform various operations on wave functions or kets, like differentiation, multiplication *etc*. The result of such an operation may be:

- The *same* function or ket, multiplied by a constant. In this case we say the function is an EIGENFUNCTION of that operator and the constant is the EIGENVALUE associated with that eigenfunction.

$$\hat{H}\varphi(r,\theta,\phi) = E\varphi(r,\theta,\phi) \qquad \hat{H}\left|\varphi_{n,\ell,m_\ell,m_s}\right\rangle = E_{n,\ell,m_\ell,m_s}\left|\varphi_{n,\ell,m_\ell,m_s}\right\rangle$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sin(kx) = \frac{\hbar^2 k^2}{2m}\sin(kx)$$

OPERATORS

are mathematical instructions that represent physical quantities like energy or momentum. They perform various operations on wave functions or kets, like differentiation, multiplication *etc*. The result of such an operation may be:

- A *different* function or ket (or sum of kets) multiplied by a constant. In this case we say the function is NOT an eigenfunction of that operator.

$$\hat{p}\varphi(r) \neq p\varphi(r)$$

$$\frac{\hbar}{i}\frac{d}{dx}\sin(kx) = \frac{\hbar k}{i}\cos(kx)$$

OPERATORS

can also be represented as matrices. In this case, the operator is just a table of projections!

$$H = \begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle & \langle 1|H|3\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle & \langle 2|H|3\rangle \\ \langle 3|H|1\rangle & \langle 3|H|2\rangle & \langle 3|H|3\rangle \end{pmatrix}$$

Now IF …..

$$\hat{H}|1\rangle = E_1|1\rangle$$
$$\hat{H}|2\rangle = E_2|2\rangle$$
$$\hat{H}|3\rangle = E_1|3\rangle$$

Then what is the H matrix?

OPERATORS

as matrices. What are the eigenvectors?

$$H = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix}$$

OPERATORS

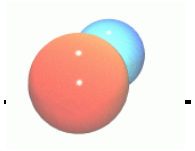
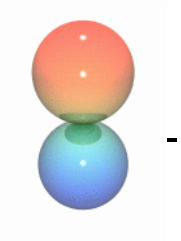
can also be represented as matrices. A square matrix acts on a column vector or ket. The result of such an operation may be:

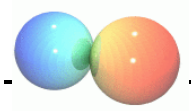
- The *same* column vector or ket, multiplied by a constant. In this case we say the function is an EIGENVECTOR of that operator and the constant is the EIGENVALUE associated with that eigenvector.

$$\begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = E_1 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = E_2 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

If an OPERATOR acts on a ket, to produce a new ket, we can project the new ket onto some bra. Choose the kets

$$\left| \text{  } \right\rangle \qquad \left| p_x \right\rangle = \frac{1}{\sqrt{2}} \left[\left| Y_{1,-1} \right\rangle - \left| Y_{1,1} \right\rangle \right] \qquad \left| \text{  } \right\rangle$$

$$\left| \text{  } \right\rangle \qquad \left| p_y \right\rangle = \frac{i}{\sqrt{2}} \left[\left| Y_{1,-1} \right\rangle + \left| Y_{1,1} \right\rangle \right] \qquad \left| p_z \right\rangle = \left| Y_{1,0} \right\rangle$$

$$\hat{L}^2 \left| p_x \right\rangle = 2\hbar^2 \left| p_x \right\rangle$$

$$\hat{L}^2 \left| p_y \right\rangle = 2\hbar^2 \left| p_y \right\rangle$$

$$\hat{L}^2 \left| p_z \right\rangle = 2\hbar^2 \left| p_z \right\rangle$$

These are (degenerate) eigenfunctions of the "angular-momentum-squared" operator. The states have definite angular momentum.

Now project these new kets onto the three bras. You get 9 numbers …. Organize them in a matrix

Represent the L^2 OPERATOR in the basis of $|p_x\rangle$, $|p_y\rangle$, $|p_z\rangle$,

$$\langle p_x | \hat{L}^2 | p_z \rangle = \langle p_x | 2\hbar^2 | p_z \rangle = \langle p_x | p_z \rangle = 0$$

$$\langle p_y | \hat{L}^2 | p_z \rangle = 0$$

$$\langle p_z | \hat{L}^2 | p_z \rangle = 2\hbar^2$$

$$\hat{L}^2 = \begin{matrix} \langle p_x | \\ \langle p_y | \\ \langle p_z | \end{matrix} \begin{matrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{matrix} 2\hbar^2 \qquad \begin{matrix} |p_x\rangle & |p_y\rangle & |p_z\rangle \end{matrix}$$

Sutton 2.13

$$\hat{L}^2 = \begin{pmatrix} L_{11}^2 & L_{12}^2 & L_{13}^2 \\ L_{21}^2 & L_{22}^2 & L_{23}^2 \\ L_{31}^2 & L_{32}^2 & L_{33}^2 \end{pmatrix}$$

Represent the L_z OPERATOR in the basis of $|p_x\rangle$, $|p_y\rangle$, $|p_z\rangle$,

$$\langle p_x | \hat{L}_z | p_z \rangle = \langle p_x | 0\hbar | p_z \rangle = 0$$

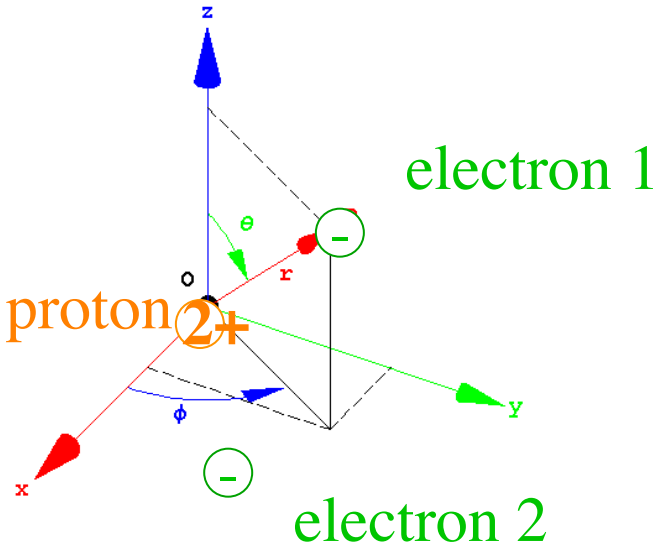
$$\hat{L}_z | p_x \rangle = \frac{\hbar}{\sqrt{2}} \left[-|Y_{1,-1}\rangle - |Y_{1,1}\rangle \right] = i\hbar | p_y \rangle$$

$$\hat{L}_z | p_y \rangle = \frac{i\hbar}{\sqrt{2}} \left[-|Y_{1,-1}\rangle + |Y_{1,1}\rangle \right] = -i\hbar | p_x \rangle$$

$$\hat{L}_z = \hbar \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Multi-electron Atoms

Much more complicated: *e-p; e-e* interactions change Schrödinger equation.
We don't need to worry too much about all of this.



$$\hat{H}\varphi(\vec{r}_1,\vec{r}_2) = E\varphi(\vec{r}_1,\vec{r}_2)$$

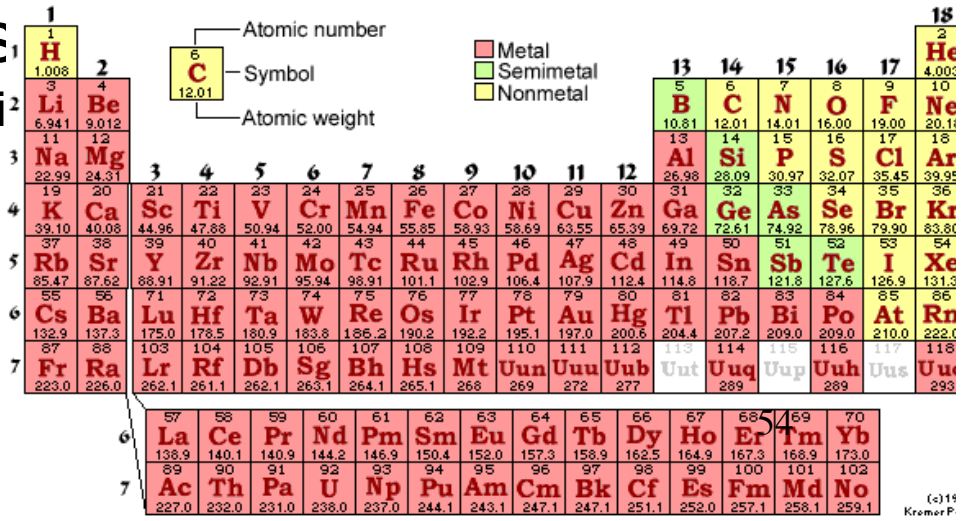
6 coordinates, not 3
(plus spin)

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

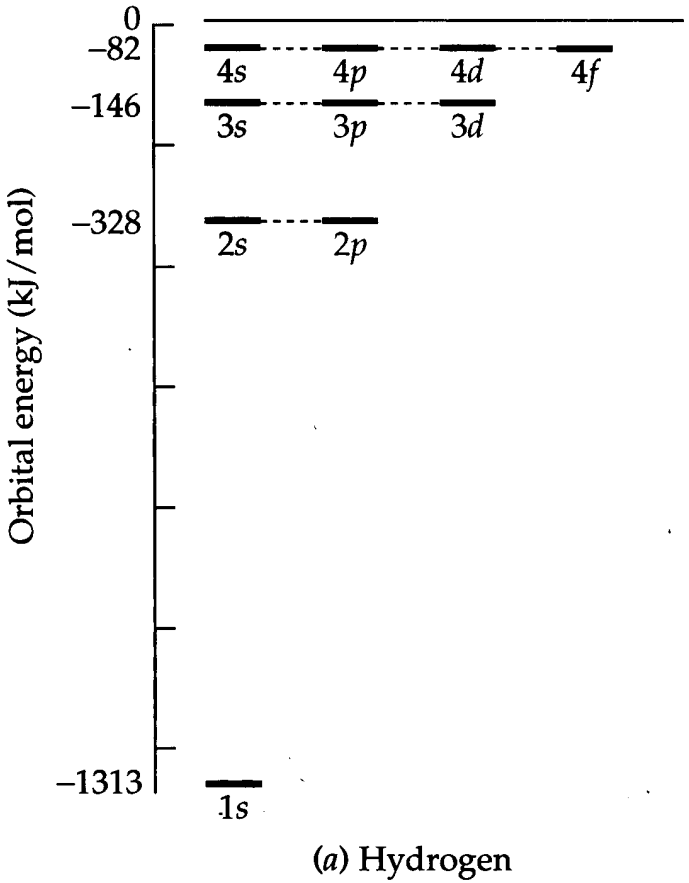
Multi-electron Atoms

- Much more complicated: *e-p; e-e* interactions change Schrödinger equation
- Radial wave functions change, but angular character is very similar to H atom wave functions
- Still makes sense to talk about *s*, *p*, *d*, *f* orbitals
- Energy levels no longer degenerate w.r.t. *n*
- Leads to consistent picture of elements - periodic table - with *ns*, *np*, *etc* orbitals filled with 2 electrons each (spin) in accordance with Pauli exclusion principle and Hund's rules

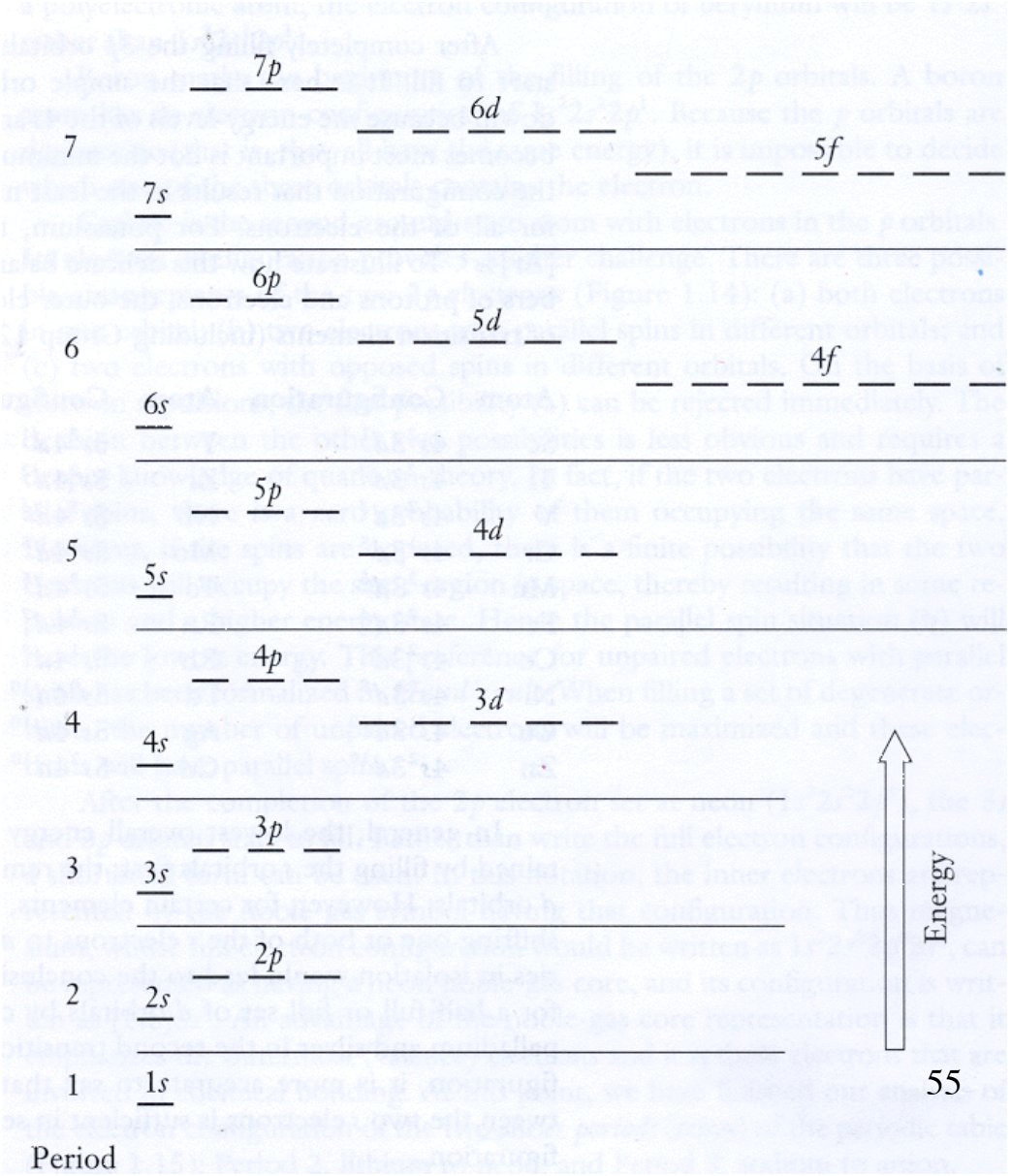
Sutton Table 1.2 for electronic configurati



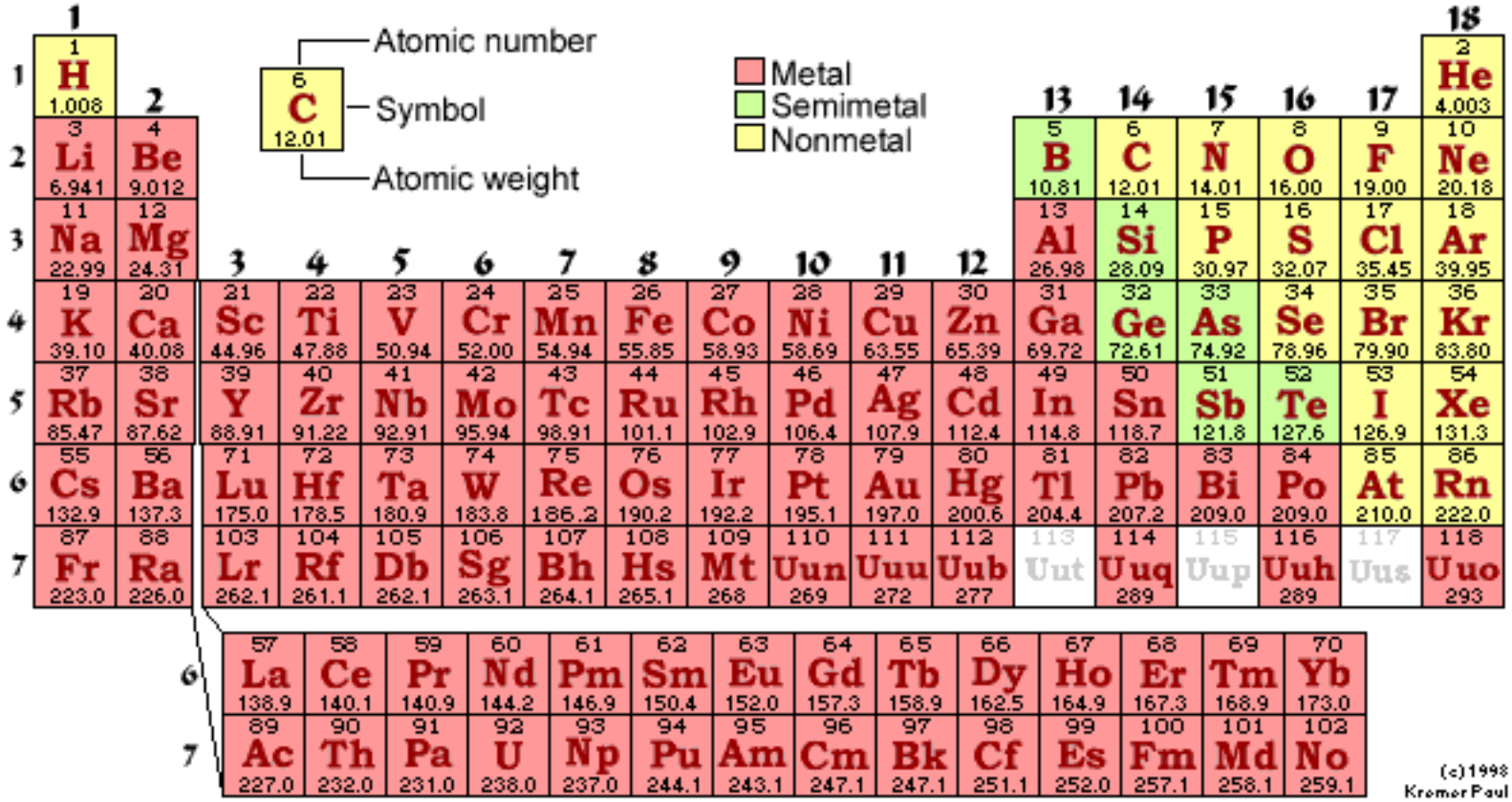
Multi-electron atoms - some *n*-degeneracy is lifted



(*a*) Hydrogen



Multi-electron Atoms



http://www.vcs.ethz.ch/chemglobe/ptoe/

Multi-electron Atoms

TABLE 1.2 The Ground-State Electronic Configurations of the Smallest Atoms

Atom	Name of element	Atomic number	1*s*	2*s*	2p_x	2p_y	2p_z	3*s*
H	Hydrogen	1	↑					
He	Helium	2	↑↓					
Li	Lithium	3	↑↓	↑				
Be	Beryllium	4	↑↓	↑↓				
B	Boron	5	↑↓	↑↓	↑			
C	Carbon	6	↑↓	↑↓	↑	↑		
N	Nitrogen	7	↑↓	↑↓	↑	↑	↑	
O	Oxygen	8	↑↓	↑↓	↑↓	↑	↑	
F	Fluorine	9	↑↓	↑↓	↑↓	↑↓	↑	
Ne	Neon	10	↑↓	↑↓	↑↓	↑↓	↑↓	
Na	Sodium	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑