

PH575 Spring 2019

Review Lecture #1a

Complex numbers

Complex numbers

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

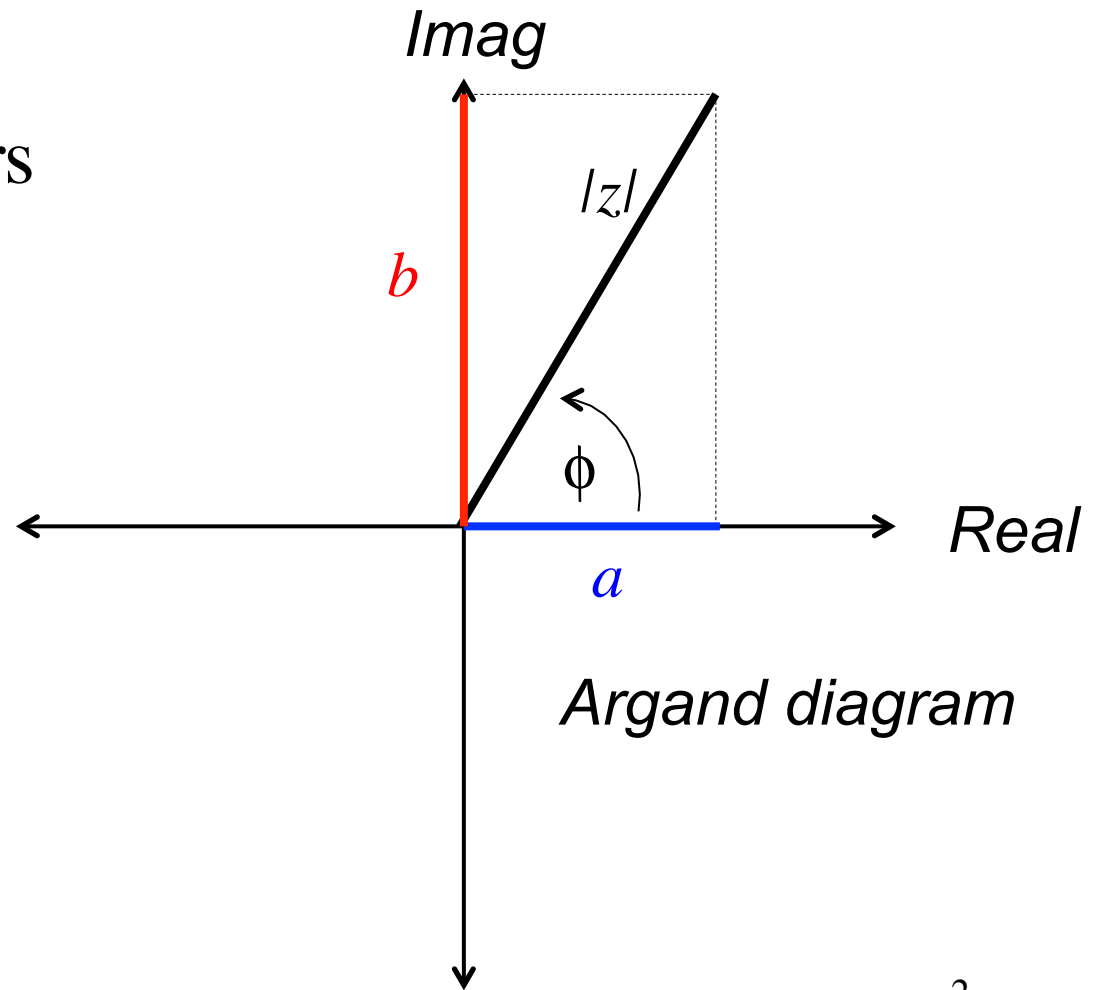
$$z = a + ib$$

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

$$\left. \begin{array}{l} \operatorname{Re}(z) = a \\ \operatorname{Im}(z) = b \end{array} \right\} \text{real numbers}$$

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

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



Euler's relation

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

Consistency argument

$$z = a + ib$$

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

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:

$$b = |z|\sin\phi$$

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

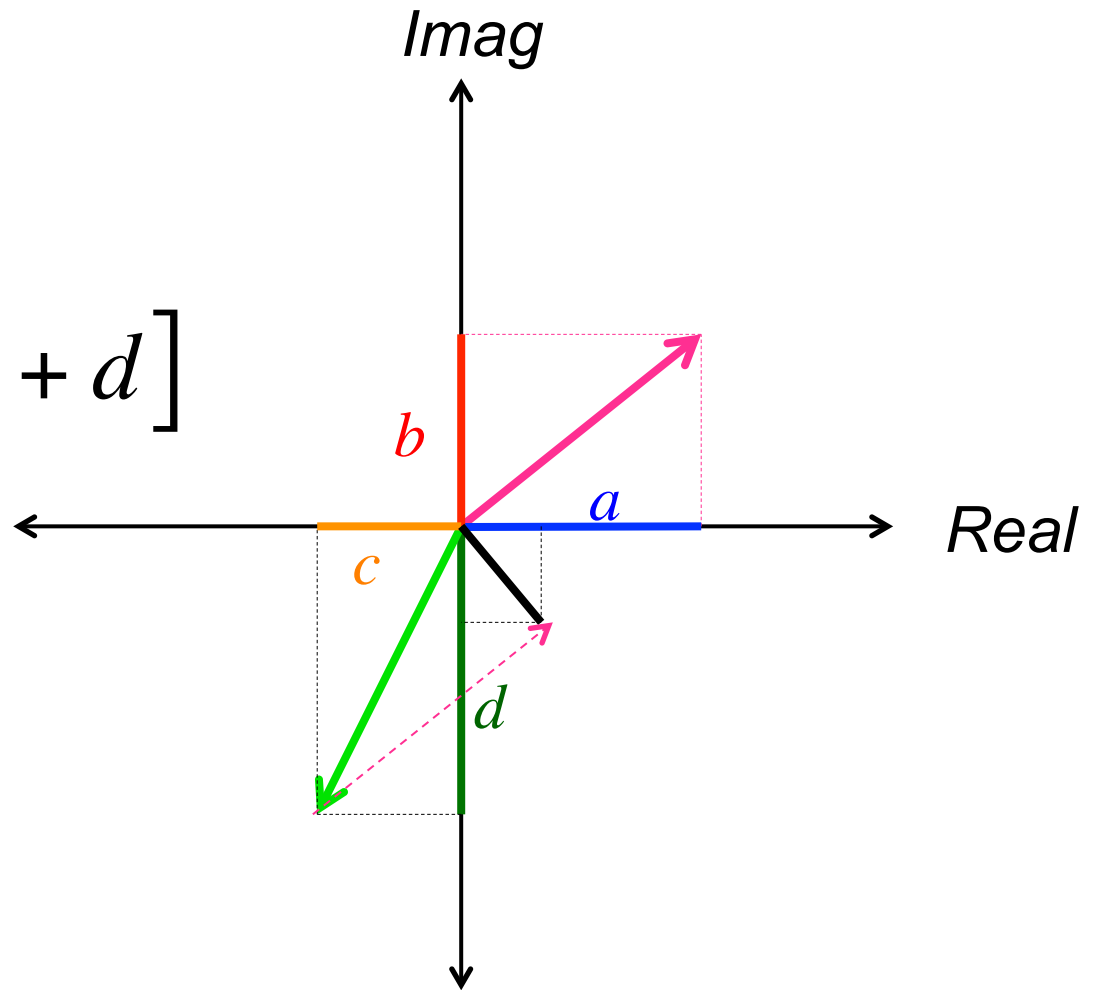
$$\tan\phi = \frac{b}{a}$$

Adding complex numbers is easy in rectangular form

$$z = a + ib$$

$$w = c + id$$

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

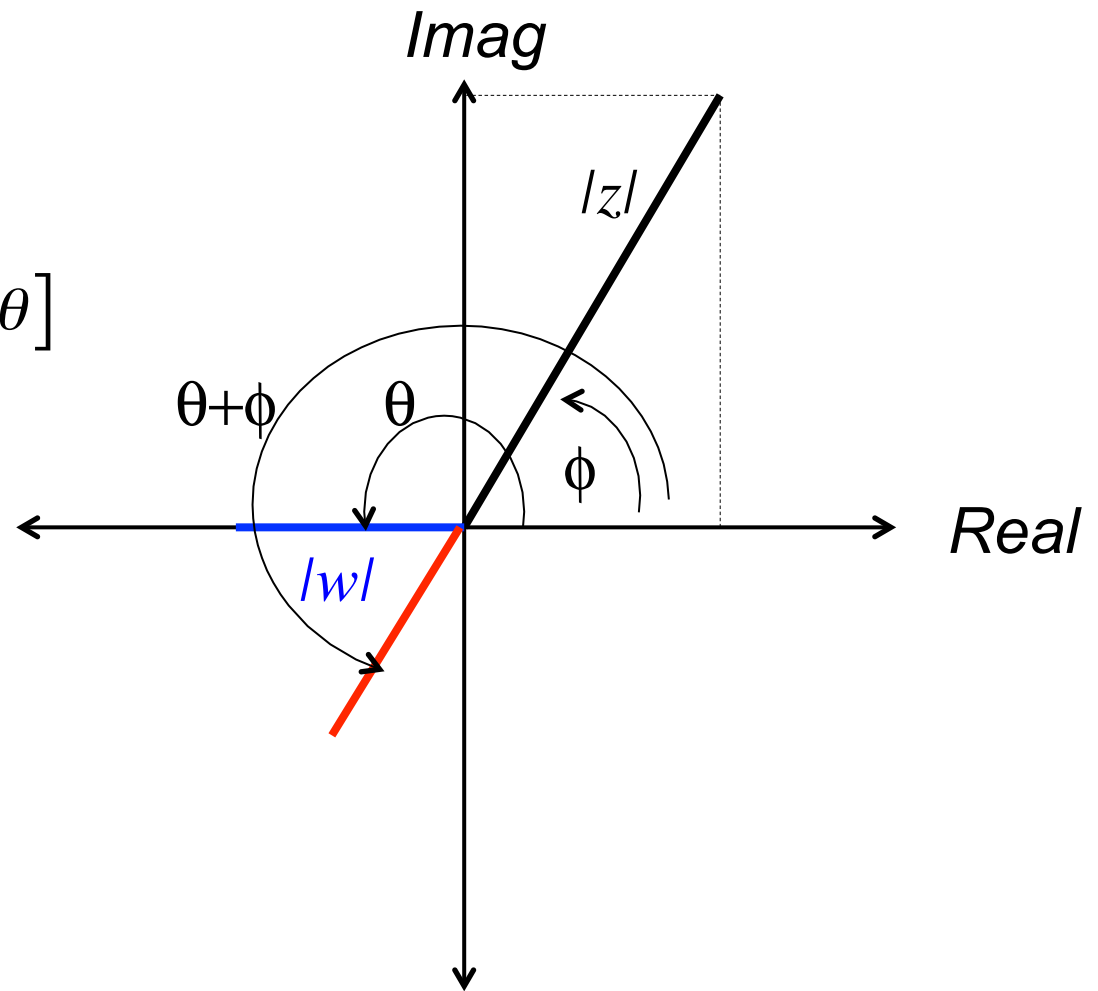


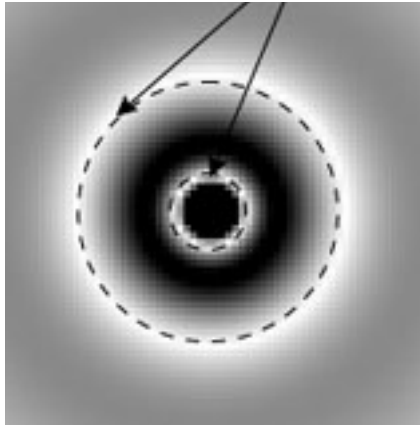
Multiplication and division of complex numbers is easy in *polar* form

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

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

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





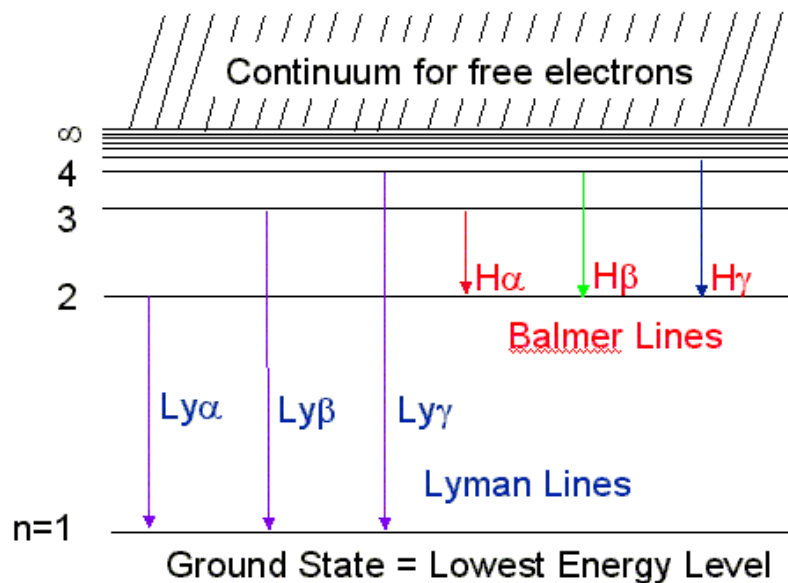
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Review Lecture #1b

Atomic orbitals, quantum numbers

Atomic states (Hydrogen Atom; wave function form)

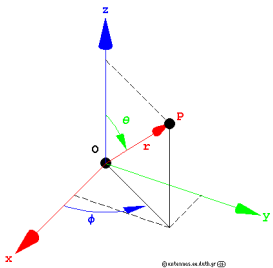
$$\hat{H}R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi) = E_{n,\ell,m_\ell,m_s}R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi)$$



$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad \text{Hamiltonian}$$

$$E_{n,\ell,m_\ell,m_s} = -\frac{e^2}{2n^2(4\pi\epsilon_0)a_0} = -\frac{13.6}{n^2} \text{ eV}$$

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

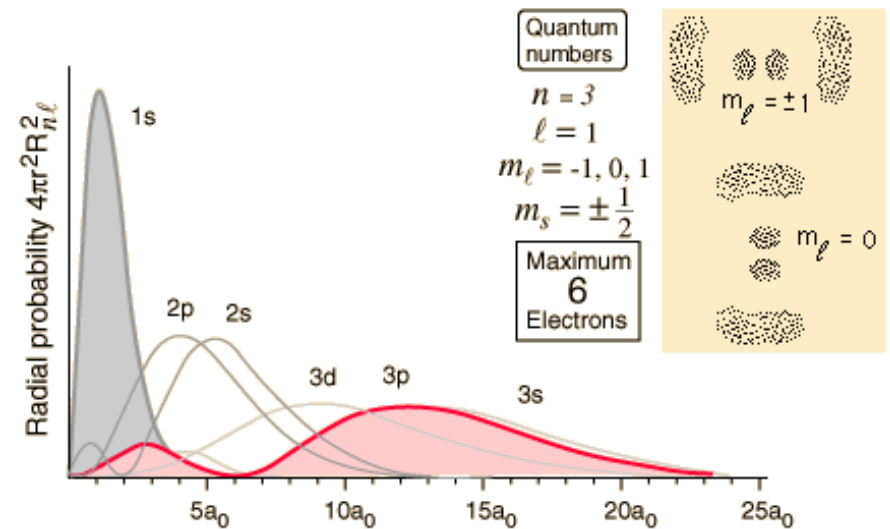
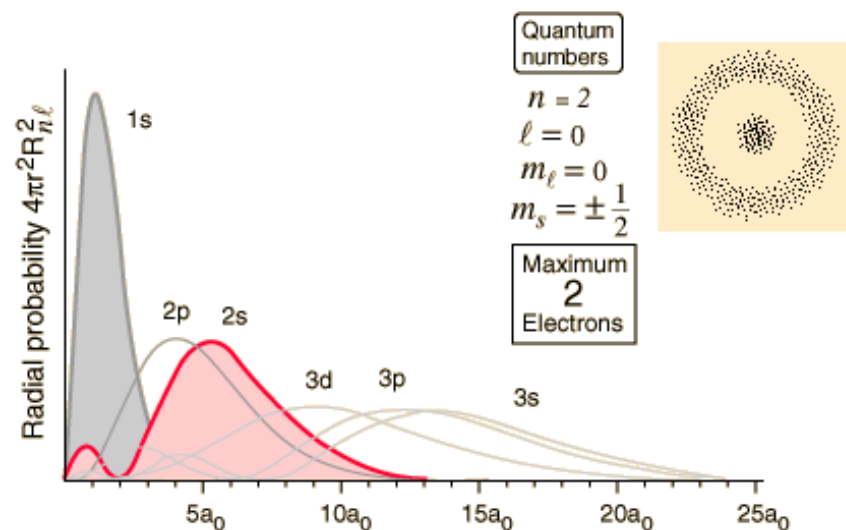
$$\left| \varphi_{n,\ell,m_\ell,m_s} \right\rangle \quad \left\langle \vec{r} \left| \varphi_{n,\ell,m_\ell,m_s} \right\rangle = R_{n,\ell}(r) Y_{\ell,m_\ell}(\theta,\phi) \chi_{m_s}$$

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

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

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

Radial wavefunction - size of electron cloud



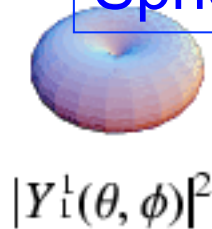
Atomic states – angular; complex (Hydrogen Atom; wave function form)



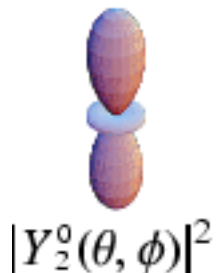
$$\left\langle \vec{r} \left| \varphi_{n,\ell,m_\ell,m_s} \right. \right\rangle = R_{n,\ell}(r) Y_{\ell,m_\ell}(\theta, \phi) \chi_{m_s}$$

Spherical harmonics - angular dependence - bonding

Page 239 of Sutton lists these functions



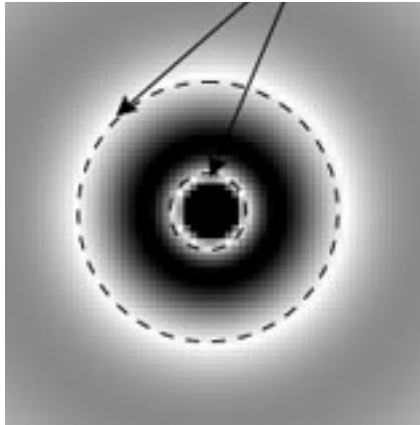
$$Y_{0,0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \quad \text{Spherically symmetric } l=0$$



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



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



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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)

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

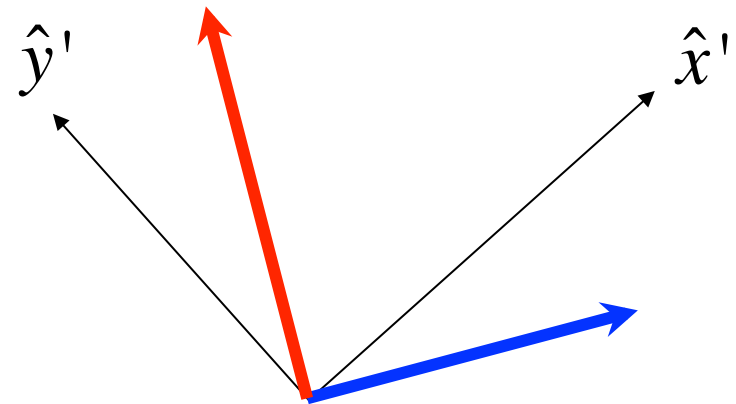
$$\sum_i |i\rangle \langle i| = 1$$

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

H atom atomic orbitals form an orthonormal set

Two **vectors** are orthogonal if

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



A **vector** is normalized if

$$\vec{a} \cdot \vec{a} = a_1 a_1 + a_2 a_2 + a_3 a_3 + \dots = 1$$

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:

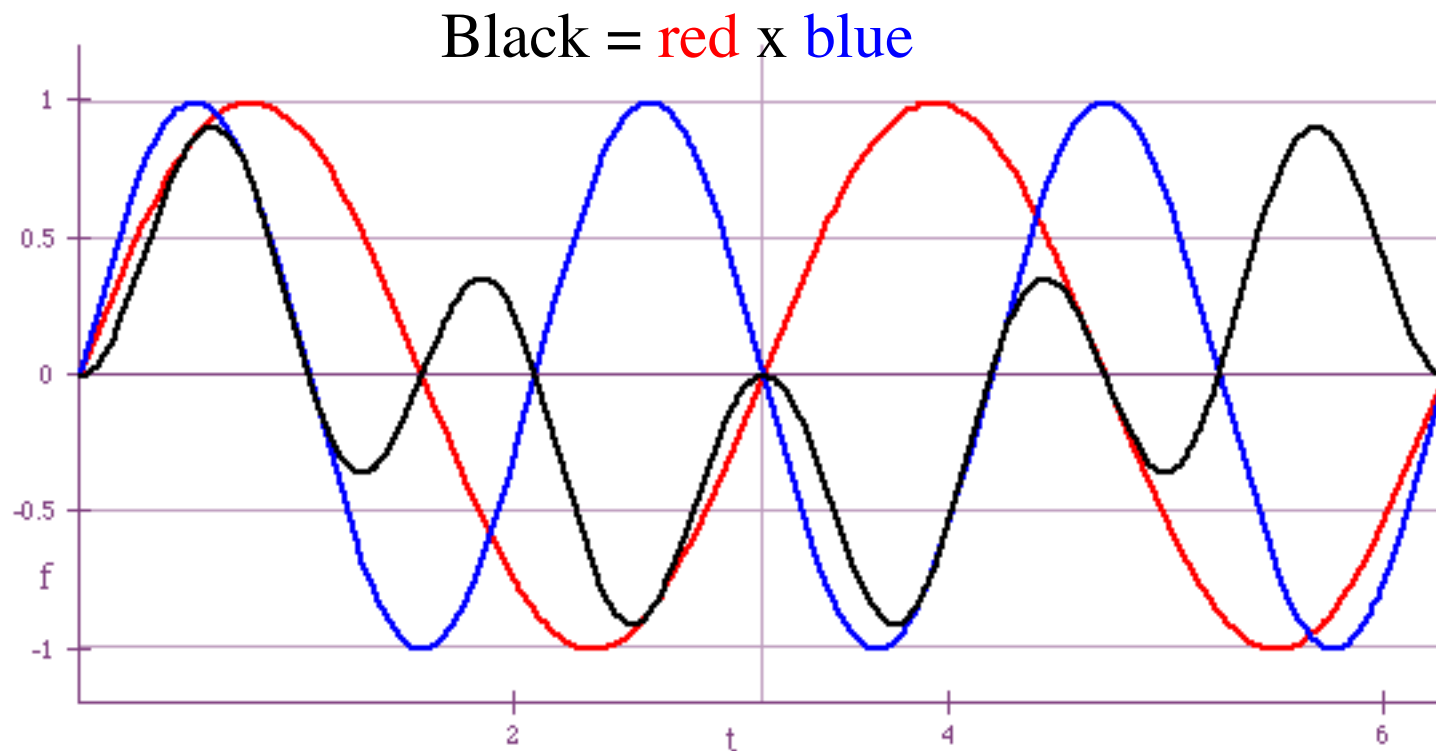
$$"f(x) \bullet g(x)" = \sum_{x_i} f^*(x_i) g(x_i)$$

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

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 $\sin(2kx)$.
The black function is $\sin(kx) * \sin(2kx)$.



- “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 $\sin(2kx)$ 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

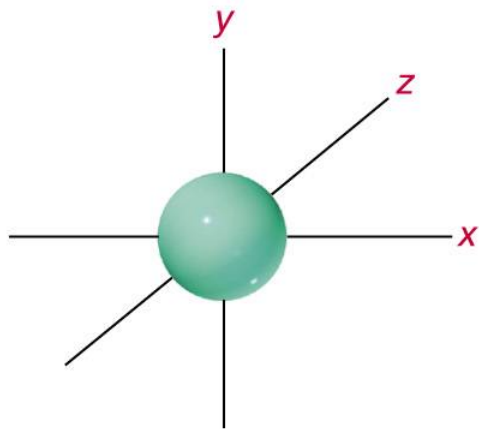
$$\begin{aligned}\langle \ell', m_{\ell}' | \ell, m_{\ell} \rangle &\equiv \int_{all} Y_{\ell', m_{\ell}'}^*(\theta, \phi) Y_{\ell, m_{\ell}}(\theta, \phi) d\Omega \\ &= \delta_{\ell\ell'} \delta_{m_{\ell} m_{\ell}'}\end{aligned}$$

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

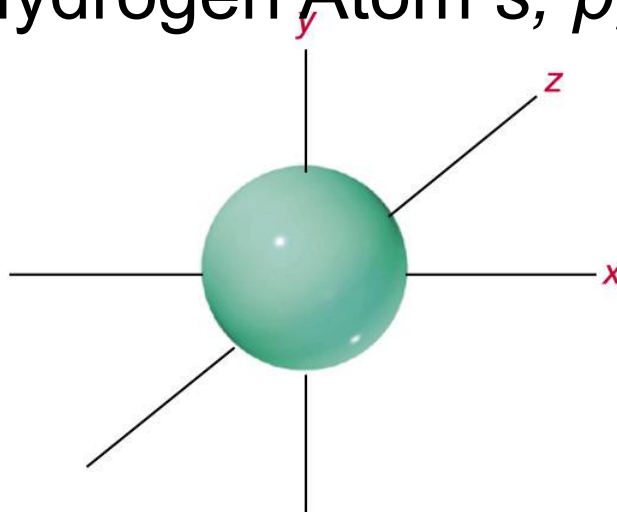
Bra = complex conjugate of ket: $\langle \ell, m_{\ell} | \doteq Y_{\ell, m_{\ell}}^*(\theta, \phi)$

$$\langle \quad | \quad \rangle = \text{integrate over all space}$$

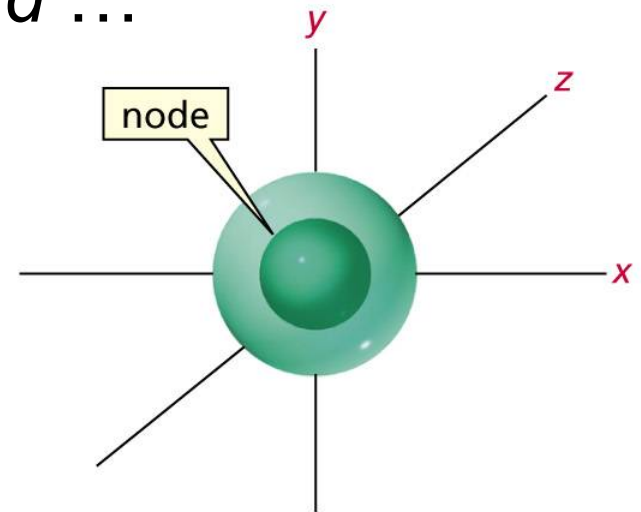
The Hydrogen Atom s , p , d ...



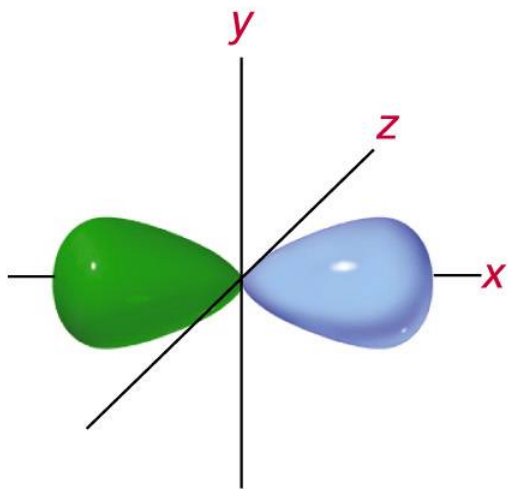
1s atomic orbital



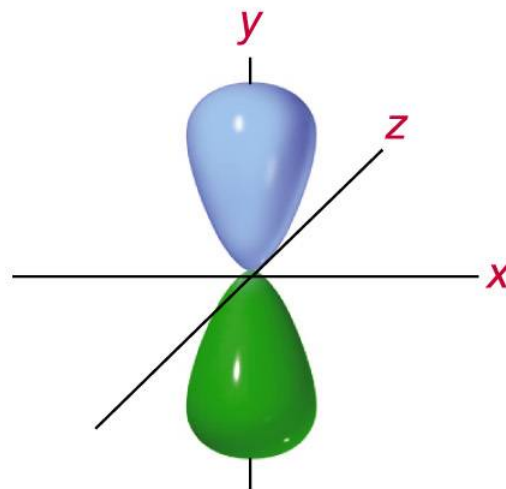
2s atomic orbital
node not shown



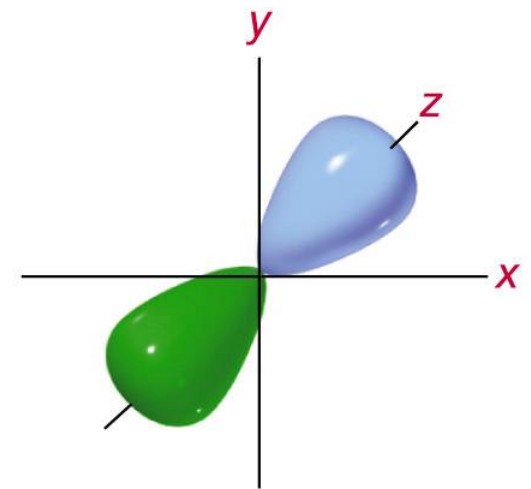
2s atomic orbital
node shown



$2p_x$ orbital

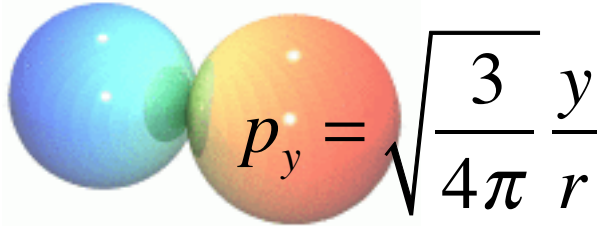


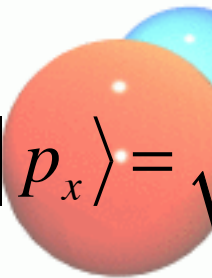
$2p_y$ orbital



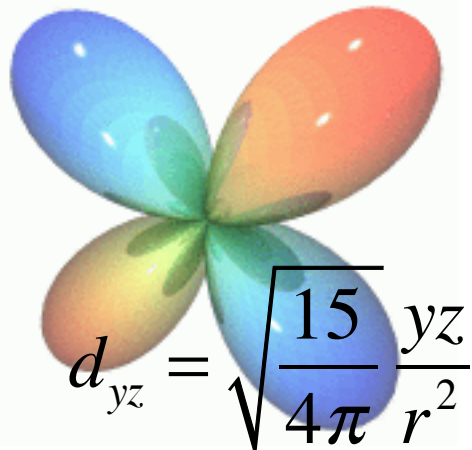
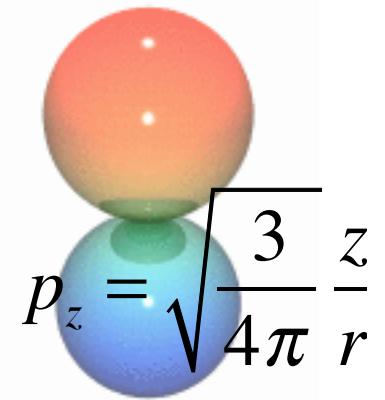
$2p_z$ orbital

The Hydrogen Atom s, p, d ...

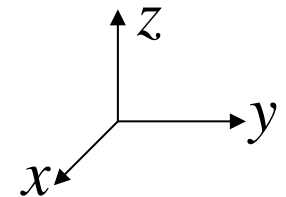
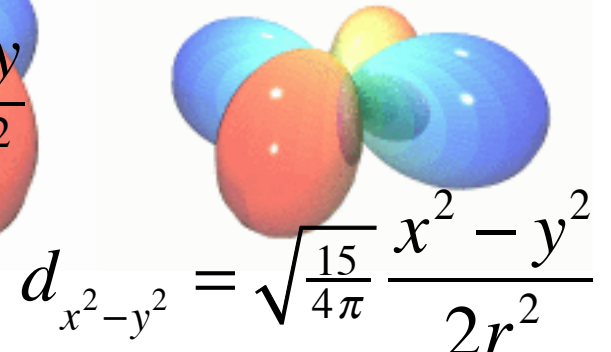
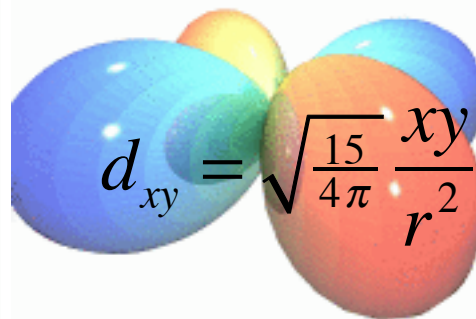
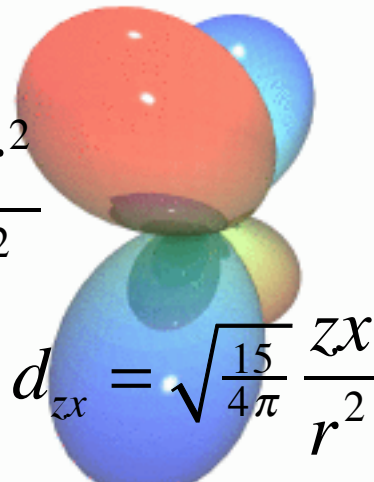
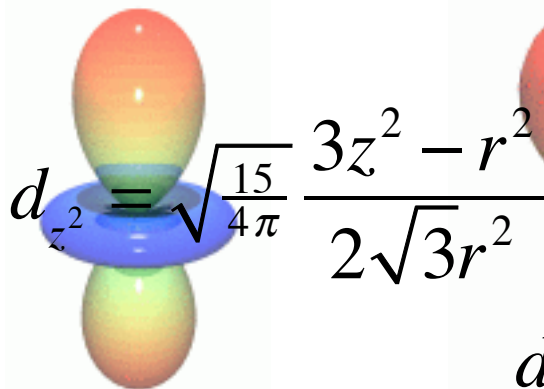




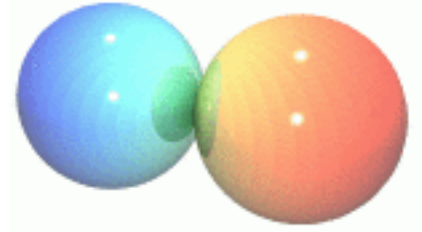
$$\langle \vec{r} | p_x \rangle = \sqrt{\frac{3}{4\pi}} R_{n,1}(r) \frac{x}{r}$$



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



p orbitals are linear combinations of Y_{1m}



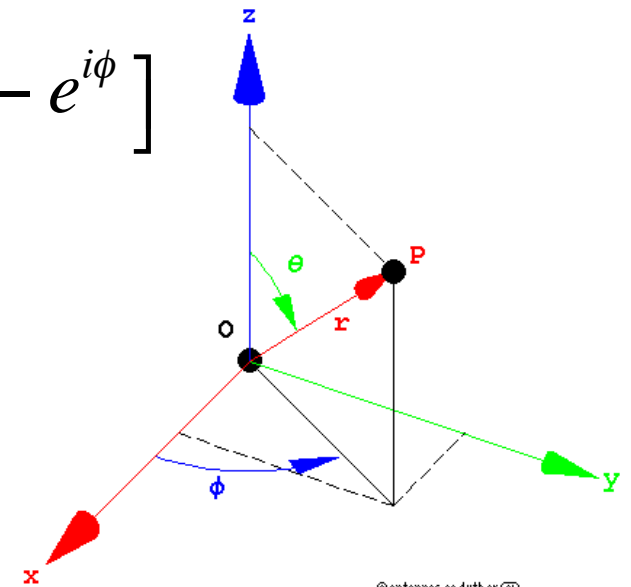
$$p_y = \sqrt{\frac{3}{4\pi}} \frac{y}{r}$$

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

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

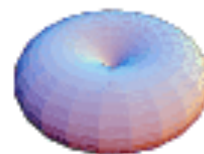
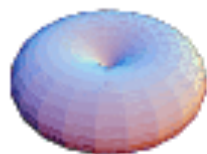
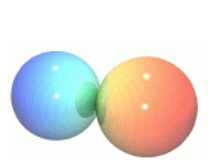
$$\frac{-2ii}{\sqrt{2}} \sqrt{\frac{3}{8\pi}} \sin \theta \sin \phi = \sqrt{\frac{3}{4\pi}} \sin \theta \sin \phi$$

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



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



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

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 $|Y_{1,0}\rangle$

Project p_y onto $Y_{1,-1}$:

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

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

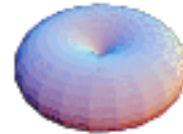
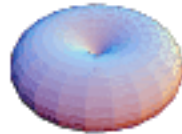
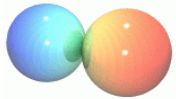
$$\langle Y_{1,-1} | p_y \rangle = \langle \text{donut} \mid \text{two lobes} \rangle = \int_{\text{volume}} Y_{1,-1}^* p_y d\Omega$$

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

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

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

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

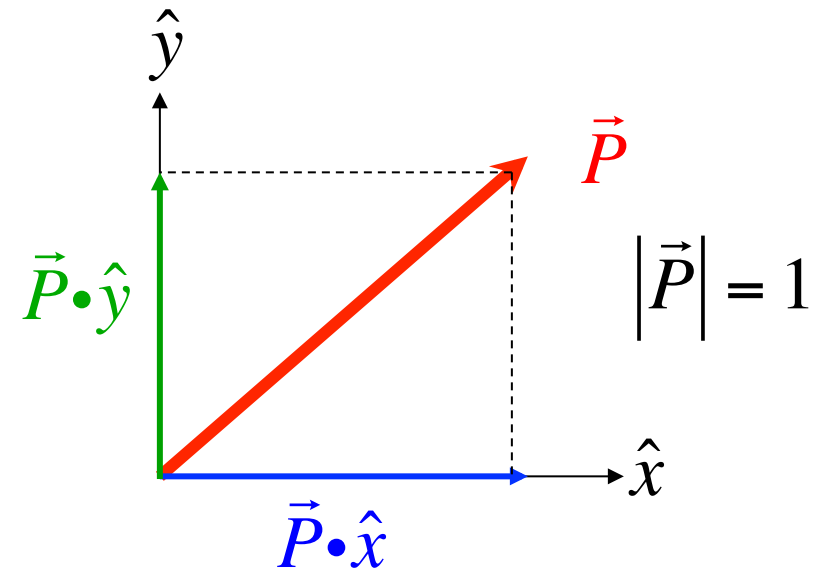
This is a **vector**, \vec{P}
represented in one
coordinate system

$$\vec{P} = \vec{P} \cdot \hat{x} \hat{x} + \vec{P} \cdot \hat{y} \hat{y}$$

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

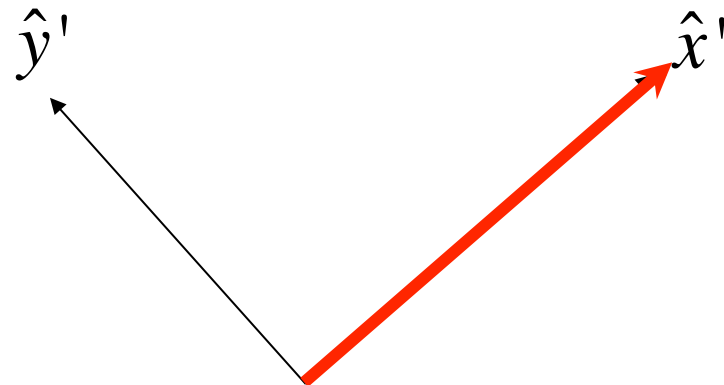
$$\vec{P} = \frac{1}{\sqrt{2}} \hat{x} + \frac{1}{\sqrt{2}} \hat{y}$$

(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)



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

$$\begin{array}{ccc} \text{Projection} & \text{Projection} & \text{Projection} \\ \text{of } |p_y\rangle \text{ on } |Y_{1,-1}\rangle & \text{of } |p_y\rangle \text{ on } |Y_{1,+1}\rangle & \text{of } |p_y\rangle \text{ on } |Y_{1,0}\rangle \end{array}$$

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*.

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

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

$$\vec{P} = (P_x, P_y) \quad \vec{Q} = (Q_x, Q_y)$$

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

- Multiply components and add the products.

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

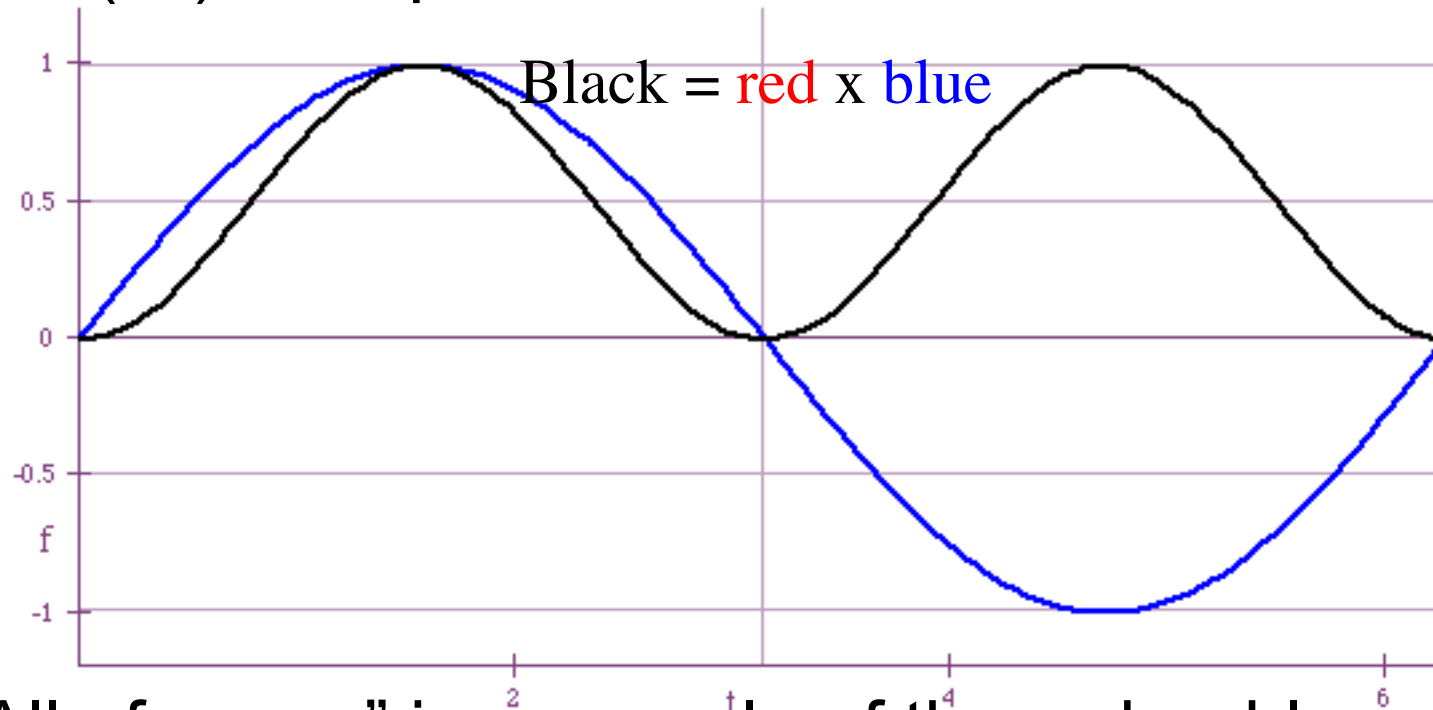
Think of a function as a vector with *many* components - each component is the value of the function at a particular point in space:

- 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.

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

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.

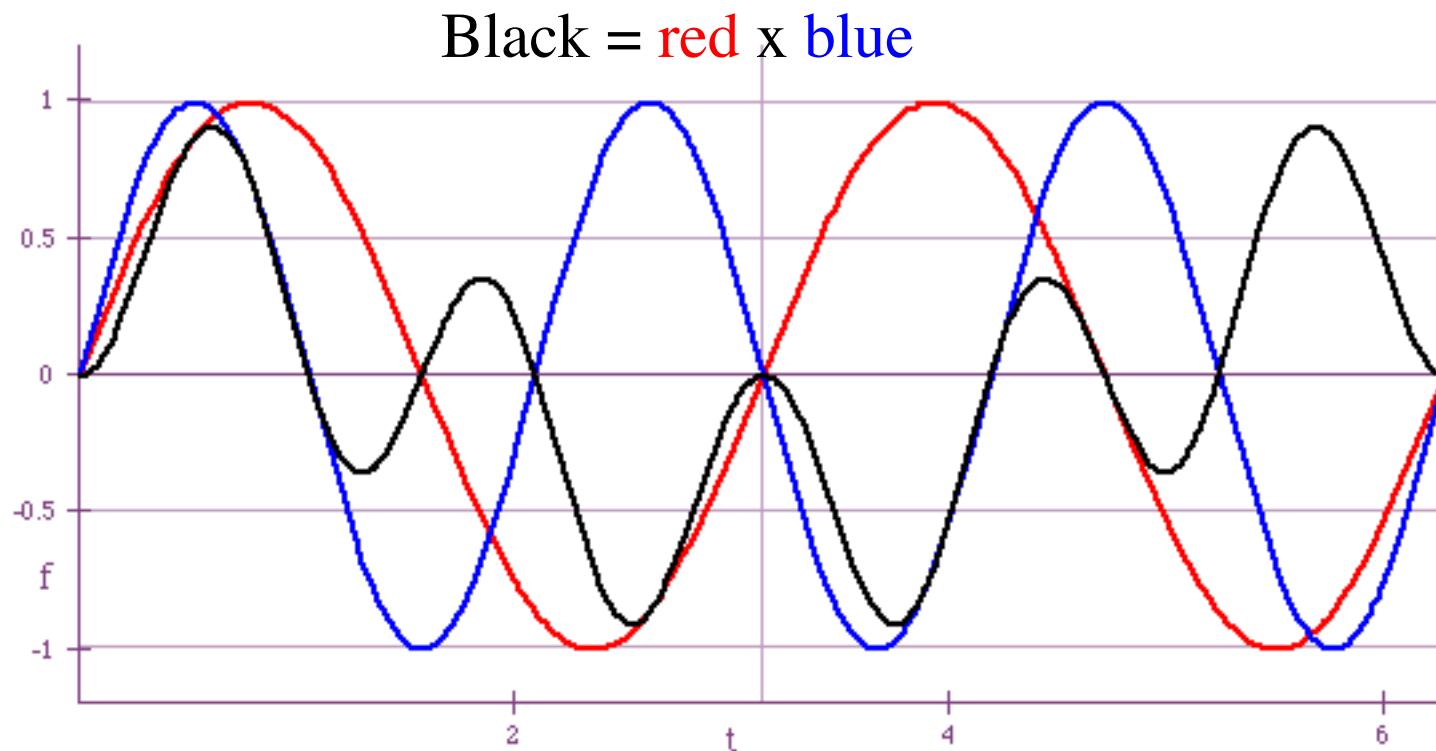


- “All of space” is one cycle of the red or blue function.
- The integral of the black function over all space is

.....
April 1, 2019

- Not zero! The projection of $\sin(kx)$ onto itself is 1!

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



- "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 $\sin(2kx)$ 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

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

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

An example with H-atom wave functions



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

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 $|Y_{1,0}\rangle$

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

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

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

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

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

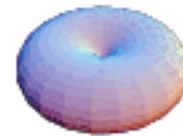
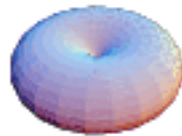
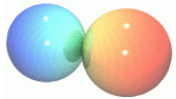
$$\langle Y_{1,-1} | p_y \rangle = \langle \text{[donut-shaped orbital]} | \text{[two-lobed orbital]} \rangle = \int_{\text{volume}} Y_{1,-1}^* p_y dV$$

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

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

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

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.

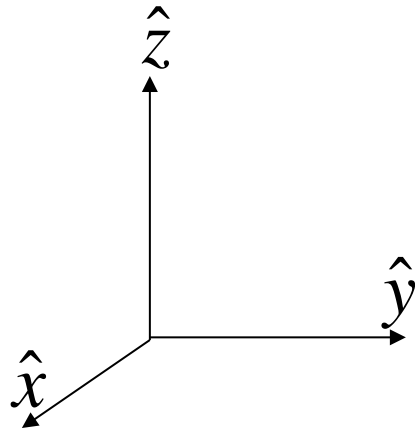


$$|p_y\rangle = \langle Y_{1,-1} | p_y \rangle |Y_{1,-1}\rangle + \langle Y_{1,+1} | p_y \rangle |Y_{1,+1}\rangle + \langle Y_{1,0} | p_y \rangle |Y_{1,0}\rangle$$

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*.

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

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

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

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

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

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

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

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

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

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

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

$$\langle p_z | p_y \rangle = \frac{i}{\sqrt{2}} \left[\underbrace{\langle Y_{1,0} | Y_{1,-1} \rangle}_0 + \underbrace{\langle Y_{1,0} | Y_{1,+1} \rangle}_0 \right] = 0$$

$$\begin{aligned}
 |p_z\rangle &= |Y_{1,0}\rangle & |p_y\rangle &= \frac{i}{\sqrt{2}} [|Y_{1,-1}\rangle + |Y_{1,1}\rangle] \\
 & & |p_x\rangle &= \frac{1}{\sqrt{2}} [|Y_{1,-1}\rangle - |Y_{1,1}\rangle]
 \end{aligned}$$

You show $\langle p_x | p_y \rangle = 0$

END OF

Backup slides on projections of functions

Spherical Harmonic functions

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

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

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

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

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

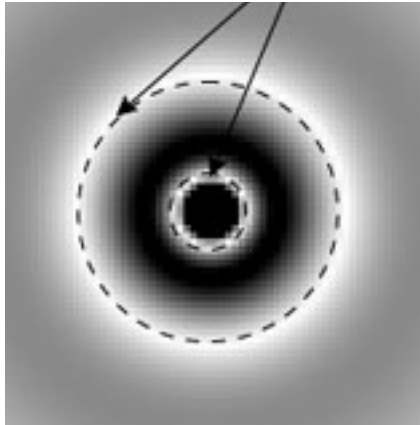
$$Y_{21} = -\sqrt{\frac{15}{8\pi}} e^{i\phi} \sin \theta \cos \theta$$

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

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.

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

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

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

$$\begin{aligned}\hat{H}|1\rangle &= E_1|1\rangle \\ \hat{H}|2\rangle &= E_2|2\rangle \\ \hat{H}|3\rangle &= E_1|3\rangle\end{aligned}$$

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

$$| \text{[diagram of two overlapping spheres, one red and one blue, side-by-side]} \rangle \quad |p_x\rangle = \frac{1}{\sqrt{2}} [|Y_{1,-1}\rangle - |Y_{1,1}\rangle]$$

$$| \text{[diagram of two overlapping spheres, one red and one blue, stacked vertically]} \rangle$$

$$| \text{[diagram of two overlapping spheres, one red and one blue, side-by-side]} \rangle \quad |p_y\rangle = \frac{i}{\sqrt{2}} [|Y_{1,-1}\rangle + |Y_{1,1}\rangle]$$

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

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

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

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

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 $|p_x\rangle$, $|p_y\rangle$, $|p_z\rangle$,

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

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

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

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 $|p_x\rangle$, $|p_y\rangle$, $|p_z\rangle$,

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

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

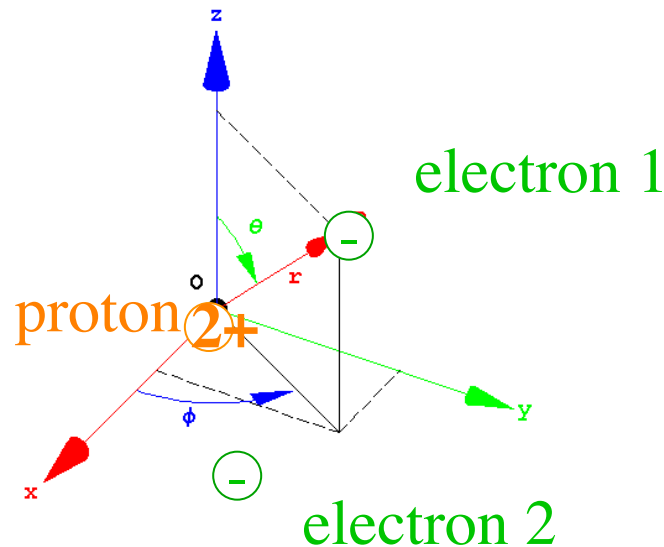
$$\hat{L}_z | p_y \rangle = \frac{i\hbar}{\sqrt{2}} [-|Y_{1,-1}\rangle + |Y_{1,1}\rangle] = -i\hbar | p_x \rangle$$

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

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.



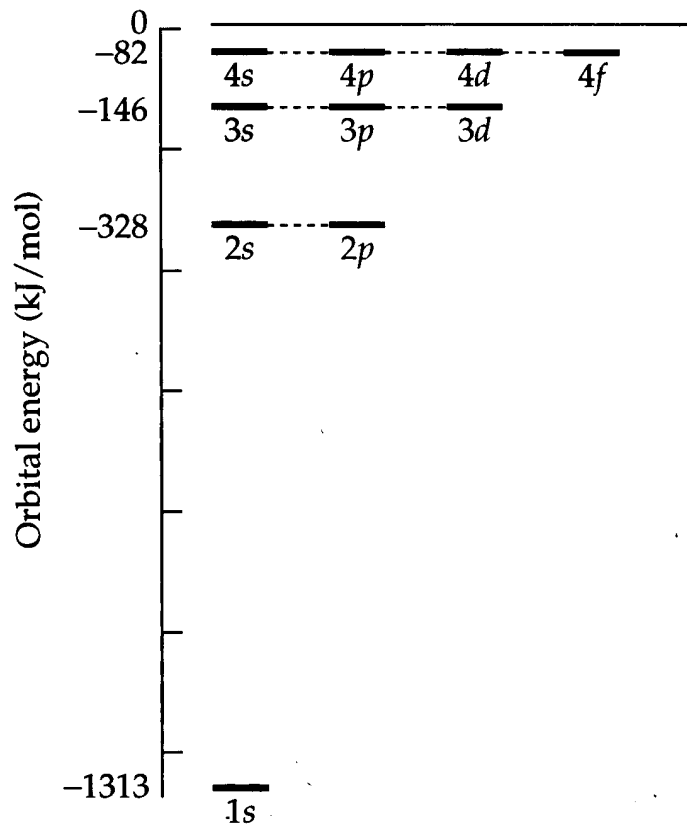
$$\hat{H}\varphi(\vec{r}_1, \vec{r}_2) = E\varphi(\vec{r}_1, \vec{r}_2)$$

↙

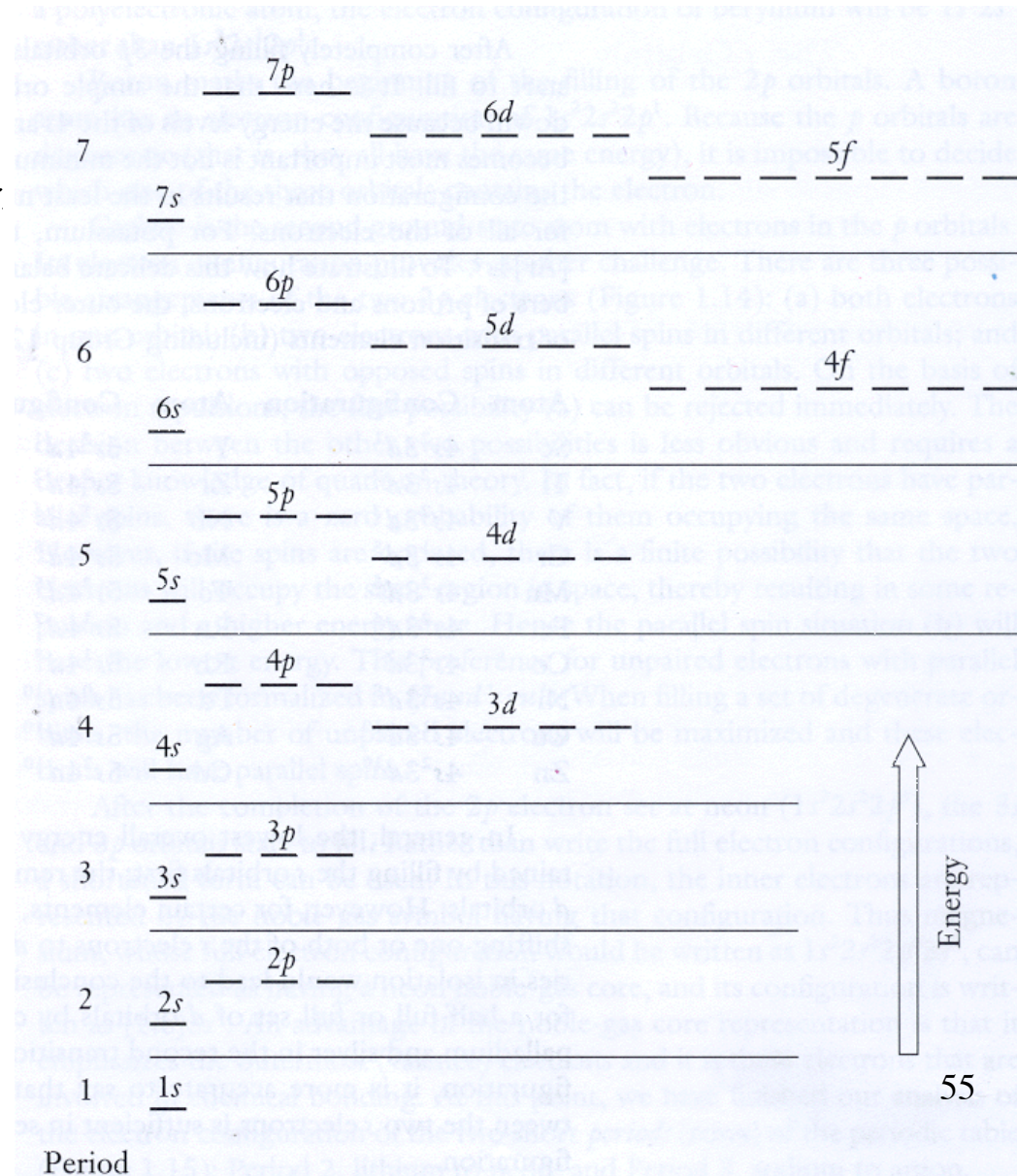
6 coordinates, not 3
(plus spin)

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

Multi-electron atoms - some n -degeneracy is lifted



(a) Hydrogen



Multi-electron Atoms

1

1

H

1.008

2

2

He

4.003

3

3

Li

6.941

4

4

Be

9.012

5

5

Na

22.99

6

6

Mg

24.31

7

7

K

39.10

8

8

Ca

40.08

9

9

Rb

85.47

10

10

Sr

87.62

11

11

Cs

132.9

12

12

Ba

137.3

13

13

Fr

223.0

14

14

Ra

226.0

15

15

Sc

44.96

16

16

Ti

47.88

17

17

V

50.94

18

18

Cr

52.00

19

19

Mn

54.94

20

20

Fe

55.85

21

21

Co

58.93

22

22

Ni

58.69

23

23

Cu

63.55

24

24

Zn

65.39

25

25

Ga

69.72

26

26

Ge

72.61

27

27

As

74.92

28

28

Se

78.96

29

29

Br

79.90

30

30

Kr

83.80

31

31

Rb

85.47

32

32

Sr

87.62

33

33

Cs

132.9

34

34

Ba

137.3

35

35

Fr

223.0

36

36

Ra

226.0

37

37

Ac

227.0

38

38

Th

232.0

39

39

Pa

231.0

40

40

U

238.0

41

41

Np

237.0

42

42

Pu

244.1

43

43

Am

243.1

44

44

Cm

247.1

45

45

Bk

247.1

46

46

Cf

251.1

47

47

Es

252.0

48

48

Fm

257.1

49

49

Md

258.1

50

50

No

259.1

51

51

La

138.9

52

52

Ce

140.1

53

53

Pr

140.9

54

54

Nd

144.2

55

55

Pm

146.9

56

56

Sm

150.4

57

57

Eu

152.0

58

58

Gd

157.3

59

59

Tb

158.9

60

60

Dy

162.5

61

61

Ho

164.9

62

62

Er

167.3

63

63

Tm

168.9

64

64

Yb

173.0

65

65

La

138.9

66

66

Ce

140.1

67

67

Pr

140.9

68

68

Nd

144.2

69

69

Pm

146.9

70

70

Sm

150.4

71

71

Eu

152.0

72

72

Gd

157.3

73

73

Tb

158.9

74

74

Dy

162.5

75

75

Ho

164.9

76

76

Er

167.3

77

77

Tm

168.9

78

78

Yb

173.0

79

79

La

138.9

80

80

Ce

140.1

81

81

Pr

140.9

82

82

Nd

144.2

83

83

Pm

146.9

84

84

Sm

150.4

85

85

Eu

152.0

86

86

Gd

157.3

87

87

Tb

158.9

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88

Dy

162.5

89

89

Ho

164.9

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Er

167.3

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Tm

168.9

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92

Yb

173.0

93

93

La

138.9

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Ce

140.1

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Pr

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Nd

144.2

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Pm

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Sm

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99

Eu

152.0

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Gd

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Tb

158.9

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102

Dy

162.5

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103

Ho

164.9

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Er

167.3

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105

Tm

168.9

106

106

Yb

173.0

107

107

La

138.9

108

108

Ce

140.1

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109

Pr

140.9

110

110

Nd

144.2

111

111

Pm

146.9

112

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Sm

150.4

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113

Eu

152.0

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Gd

157.3

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Tb

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Dy

162.5

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Ho

164.9

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Er

167.3

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Tm

168.9

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Yb

173.0

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La

138.9

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Ce

140.1

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Pr

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Nd

144.2

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Pm

146.9

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Sm

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Gd

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Dy

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Sm

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Gd

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167.3

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Tm

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Yb

173.0

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La

138.9

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Ce

140.1

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Pr

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Nd

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Pm

146.9

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Sm

150.4

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Eu

152.0

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Gd

157.3

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Tb

158.9

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172

Dy

162.5

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Ho

164.9

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Er

167.3

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175

Tm

168.9

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176

Yb

173.0

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La

138.9

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Ce

140.1

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179

Pr

140.9

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180

Nd

144.2

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Pm

146.9

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Sm

150.4

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Eu

152.0

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Gd

157.3

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Tb

158.9

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Dy

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187

Ho

164.9

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Er

167.3

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189

Tm

168.9

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Yb

173.0

191

191

La

138.9

192

192

Ce

140.1

193

193

Pr

140.9

194

194

Nd

144.2

195

195

Pm

146.9

196

196

Sm

150.4

197

197

Eu

152.0

198

198

Gd

157.3

199

199

Tb

158.9

200

200

Dy

162.5

201

201

Ho

164.9

202

202

Er

167.3

203

203

Tm

168.9

204

204

Yb

173.0

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205

La

138.9

206

206

Ce

140.1

207

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Pr

140.9

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Nd

144.2

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Pm

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Sm

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Eu

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Yb

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La

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Ce

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Pm

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Sm

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Sm

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Eu

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Yb

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Gd

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Tb

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Dy

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Ho

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Tm

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Yb

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La

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Ce

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Pr

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Nd

144.2

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Pm

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Sm

Multi-electron Atoms

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

| Atom | Name of element | Atomic number | 1s | 2s | 2p _x | 2p _y | 2p _z | 3s |
|------|-----------------|---------------|----|----|-----------------|-----------------|-----------------|----|
| 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 | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ |