What did we learn last day?

1. Learnt Atomic Orbitals (AOs) are 'Stationary states', corresponding to standing waves created by the confinement of the electron by the proton in H atom model.

2. Learnt what are standing waves and wave packets how they correspond to electrons under confinement using Uncertainty principle and De Broglie relation.

3. Learnt how stationary states correspond to standing waves (AOs) and represent 2D probability surfaces Giving rise to 2D nodes in AOs.

What did we learn last day?

4. Learnt to use symmetry arguments (Action principle) to arrive at the idea of 'Stationary states', corresponding to standing waves created by the confinement of the electron by the proton in H atom model (approximated by particle in a box).

5. Wrote the Schroedinger equation and came to the idea of principal quantum number (n) from particle in a box.

$$\hat{H}\psi = E.\psi$$

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

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \quad \textbf{and} \quad E_n = \frac{n^2h^2}{8mL^2}$$

What will we learn today?

We will work with Schroedinger equation and come to probe the nature of the Atomic Orbitals as Probability Surfaces.

$$\hat{H}\psi = E.\psi$$

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

What will we learn today?

Problem with this approach:

$$\widehat{H}\psi = E.\psi$$

$$\widehat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)$$

Schrödinger equation of H-Atom: Cartesian Coordinates

$$\hat{H}\psi(x,y,z) = E.\psi(x,y,z)$$

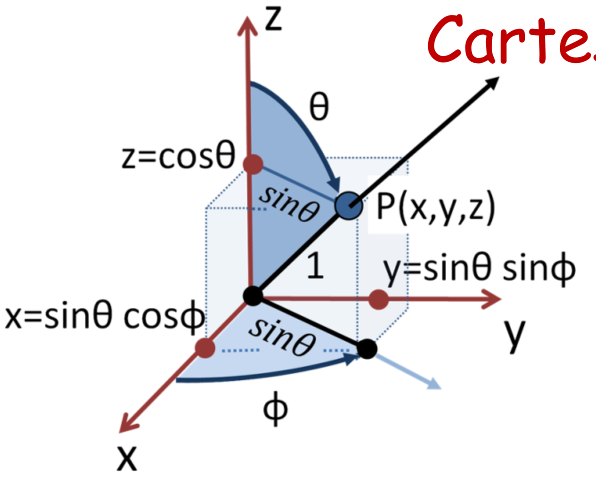
Eigen Value

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

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) - \frac{e^2}{(x^2+y^2+z^2)^{1/2}}\psi(x,y,z) = E.\psi(x,y,z)$$

Road-Block: *Symmetry violation! Not Cubic but Spherical Symmetry! So need to change the coordinate system.*

Spherical Polar Coordinates

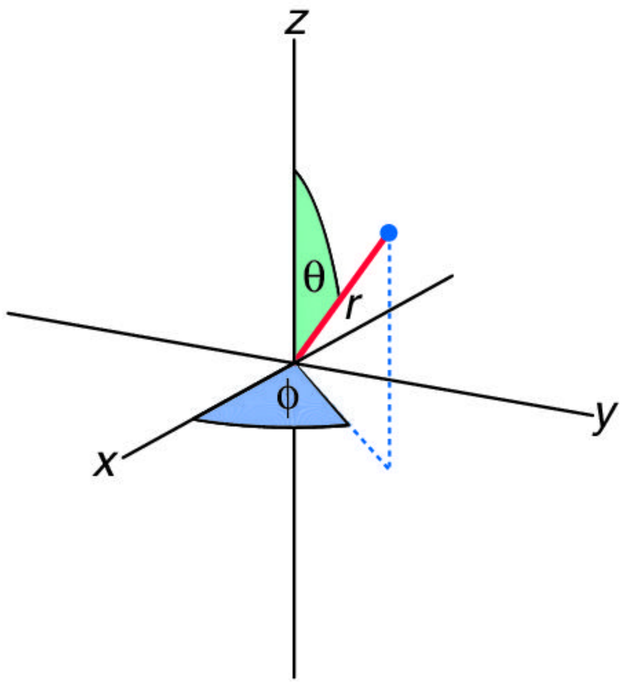


Conversion from Cartesian coordinates ?

$$x = r\sin\theta\cos\phi$$

$$y = r\sin\theta\sin\phi$$

$$z = r\cos\theta$$



- 'r' ranges from 0 to ∞
- the co-latitude θ ranges from 0 (north pole) to π (south pole)
- the azimuth ϕ ranges from 0 to 2π

What have we learned?

Why an AO has Radial and Angular Components?

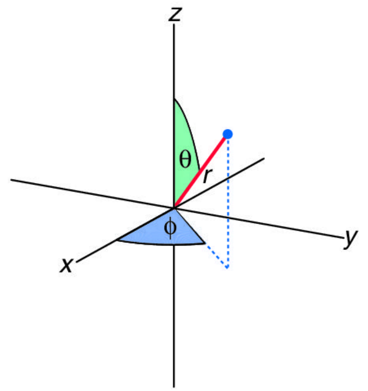
What are we going to learn?

What AOs represent from the standpoint of symmetry?

On nature of AOs.

What have we learned?

Hamiltonian in Polar Coordinates:

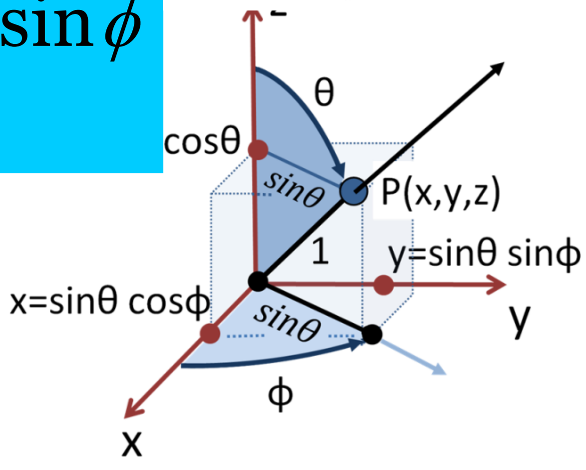


$$\widehat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)$$

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

Putting

$\widehat{H}\psi = E.\psi$, *we get* $$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{x}) + \tilde{V}(r)\psi(\boldsymbol{x}) = \tilde{E}\psi(\boldsymbol{x}).$$



Now we get $$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi).$$

Now we divide $\widehat{H}\psi$ *by* ψ *(r, ϴ, φ) and we get,*

We came up with Hamiltonian in Spherical Coordinates

$$\frac{2m}{\hbar^2}(V(r) - E)\boxed{-\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R} = \boxed{\frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta} + \boxed{\frac{1}{\Phi}\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Phi}$$

Effect of R on AOs **Effect of ϴ on AOs** **Effect of ϕ on AOs**

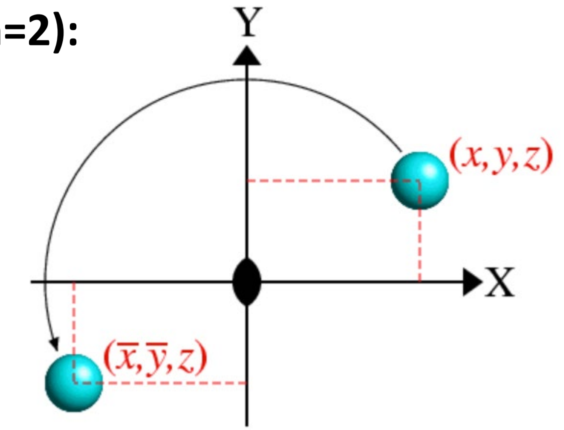
Understanding Orbitals further from Symmetry

Revisiting Uncertainty/Wave Particle Duality from Symmetry:

Symbol	Symmetry operation	Symmetry element
E	Identity (doing nothing)	----
C_n	Rotation by 360°/n	n-fold axis
σ (sigma)	Reflection	mirror plane
i	Inversion (through a center)	point
S_n	Improper rotation	n-fold axis *and* a mirror plane

Symmetry operation is a transformation of an object that leaves an object looking the same after it has been carried out.

C_2 Operation (n=2):

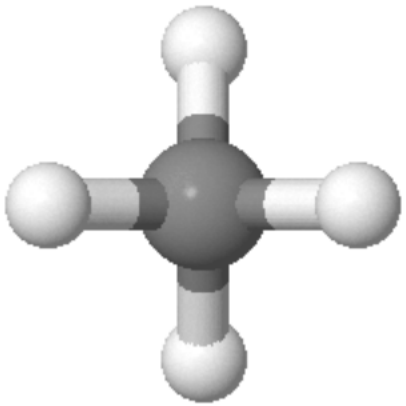


Symmetry operators transform the coordinates of one object to those of another.

Understanding Orbitals further from Symmetry

Revisiting Uncertainty/Wave Particle Duality from Symmetry:

Tetrahedral Point Group (Methane)



Methane (T_d)

Reflection Planes

- plane (σ_d) Reflect
- plane (σ_d) Reflect
- plane (σ_d) Reflect
- plane (σ_d) Reflect
- plane (σ_d) Reflect
- plane (σ_d) Reflect

Proper (C_3) Rotation Axes

- C_3 axis Rotate
- C_3 axis Rotate
- C_3 axis Rotate
- C_3 axis Rotate

Proper/Improper (C_2/S_4) Rotation Axes

- C_2 axis Rotate
- S_4 axis Rotate
- C_2 axis Rotate
- S_4 axis Rotate
- C_2 axis Rotate
- S_4 axis Rotate

Symmetry operation is a transformation of an object that leaves an object looking the same after it has been carried out.

Symmetry operators transform the coordinates of one object to those of another.

Collection of symmetry elements present in an 'Object' forms a "group", typically called a *point group*.

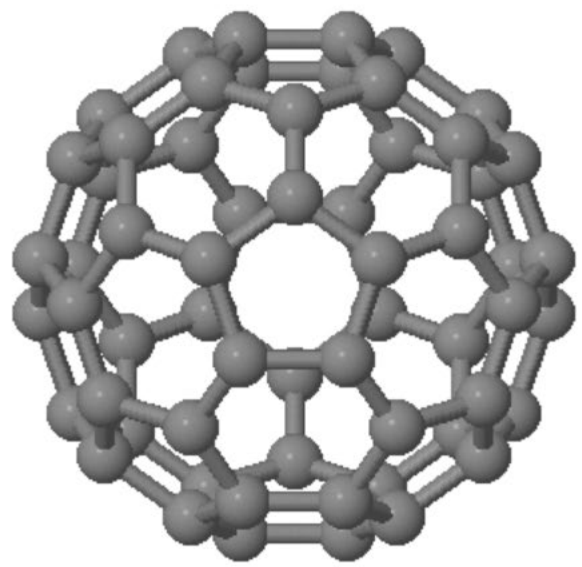
There are 32 *point groups.*
E.g., Tetrahedral (Methane)
Icosahedral (C_{60}) etc.

Visit: Symmetry @ Otterbein

Understanding Orbitals further from Symmetry

Revisiting Uncertainty/Wave Particle Duality from Symmetry:

Icosahedral Point Group (C_{60}):



Element	Operation	Element	Operation
Show All Proper		*Show All Planes*	
Show All Improper		inv ctr	Invert
C_5 axis	Rotate	plane (σ)	Reflect
C_5 axis	Rotate	plane (σ)	Reflect
C_5 axis	Rotate	plane (σ)	Reflect
C_5 axis	Rotate	plane (σ)	Reflect
C_5 axis	Rotate	plane (σ)	Reflect
C_5 axis	Rotate	plane (σ)	Reflect
C_3 axis	Rotate	plane (σ)	Reflect
C_3 axis	Rotate	plane (σ)	Reflect
C_3 axis	Rotate	plane (σ)	Reflect
C_3 axis	Rotate	plane (σ)	Reflect
C_3 axis	Rotate	plane (σ)	Reflect
C_3 axis	Rotate	plane (σ)	Reflect

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Visit: Symmetry @ Otterbein

Understanding Orbitals further from Symmetry

Revisiting Uncertainty/Wave Particle Duality from Symmetry:

Icosahedral Point Group (C_{60}) in a Character Table: Collection of Symmetry Operations and their implications:

Character table for point group I_h

I_h	E	$12C_5$	$12(C_5)^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12(S_{10})^3$	$20S_6$	15σ	linear functions, rotations	quadratic functions	cubic functions
A_g	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$	-
T_{1g}	+3	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0	-1	+3	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	-1	(R_x, R_y, R_z)	-	-
T_{2g}	+3	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	-1	+3	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0	-1	-	-	-
G_g	+4	-1	-1	+1	0	+4	-1	-1	+1	0	-	-	-
H_g	+5	0	0	-1	+1	+5	0	0	-1	+1	-	$[2z^2-x^2-y^2, x^2-y^2, xy, xz, yz]$	-
A_u	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
T_{1u}	+3	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0	-1	-3	$+2\cos(2\pi/5)$	$+2\cos(4\pi/5)$	0	+1	(x, y, z)	-	$[x(z^2+y^2), y(z^2+x^2), z(x^2+y^2)]$
T_{2u}	+3	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	-1	-3	$+2\cos(4\pi/5)$	$+2\cos(2\pi/5)$	0	+1	-	-	$[x^3, y^3, z^3]$
G_u	+4	-1	-1	+1	0	-4	+1	+1	-1	0	-	-	$[x(z^2-y^2), y(z^2-x^2), z(x^2-y^2), xyz]$
H_u	+5	0	0	-1	+1	-5	0	0	+1	-1	-	-	-

Normal Mode Symmetric w.r.t. Operations E, C_5, etc.

A_{1g} is the most Symmetric mode: Represents the Most intense Resonance of the Change in e polarizability!

e polarizability must have something to do with wavy nature and Symmetry of the operators!

Visit: Symmetry @ Otterbein

Understanding Orbitals further from Symmetry

Revisiting Uncertainty/Wave Particle Duality from Symmetry:

Commutativity, Group Theory and relation with Uncertainty:

When, A x B = B x A: Commutative

When, A x B = - B x A: Not Commutative

Think of it in terms of Symmetry Operations NOW!

→ Implication: Symmetry Operations sequence do not matter and invariance or symmetry is retained!

NOW think of it in terms of Operators (Symmetry) in Q Mech!

When, p x x = -x x p: Implies Uncertainty!

We know → **e polarizability must have something to do with wavy nature and Symmetry of the operators!**

As Linear Momentum has uncertainty so Angular Momentum will also have uncertainty! Now think of the wavy picture.

Electrons will have Stationary States (AOs) and will have 'certain' stationary 'angular' components emerging from Angular Momentum Operator (L)! So this will lead to standing waves with allowed angular states!

We came up with Hamiltonian in Spherical Coordinates

$$\frac{2m}{\hbar^2}\left(V(r)-E\right)\boxed{-\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R}=\boxed{\frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta}+\boxed{\frac{1}{\Phi}\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Phi}$$

Effect of R on AOs | Effect of ϴ on AOs | Effect of ϕ on AOs

$$x = r\sin\theta\cos\phi$$
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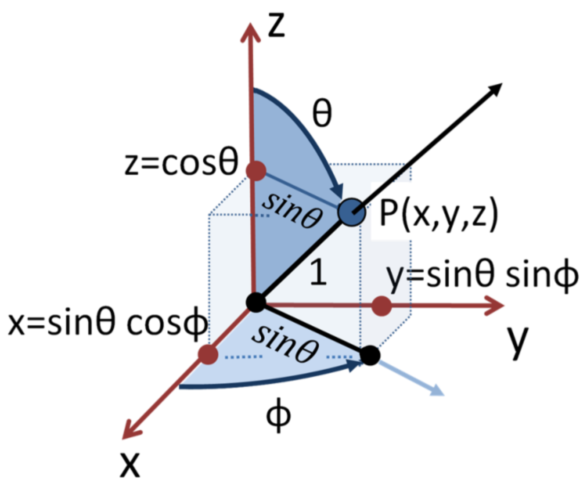

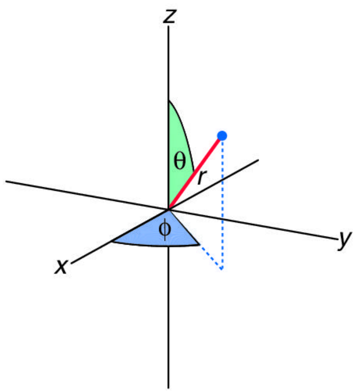

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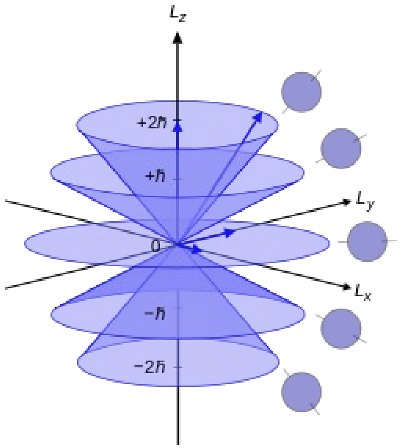

There will be finer splitting!

What we learned in today's class?

What AOs represent from the standpoint of symmetry?

On nature of AOs (Angular)...to be continued.