

Is it a Wave or a Particle?

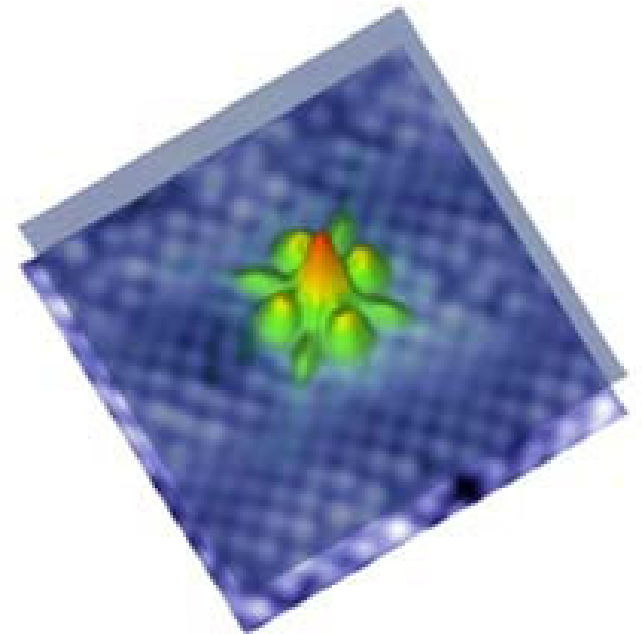
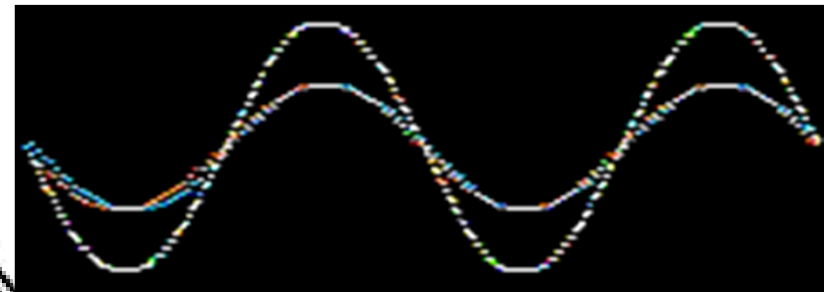
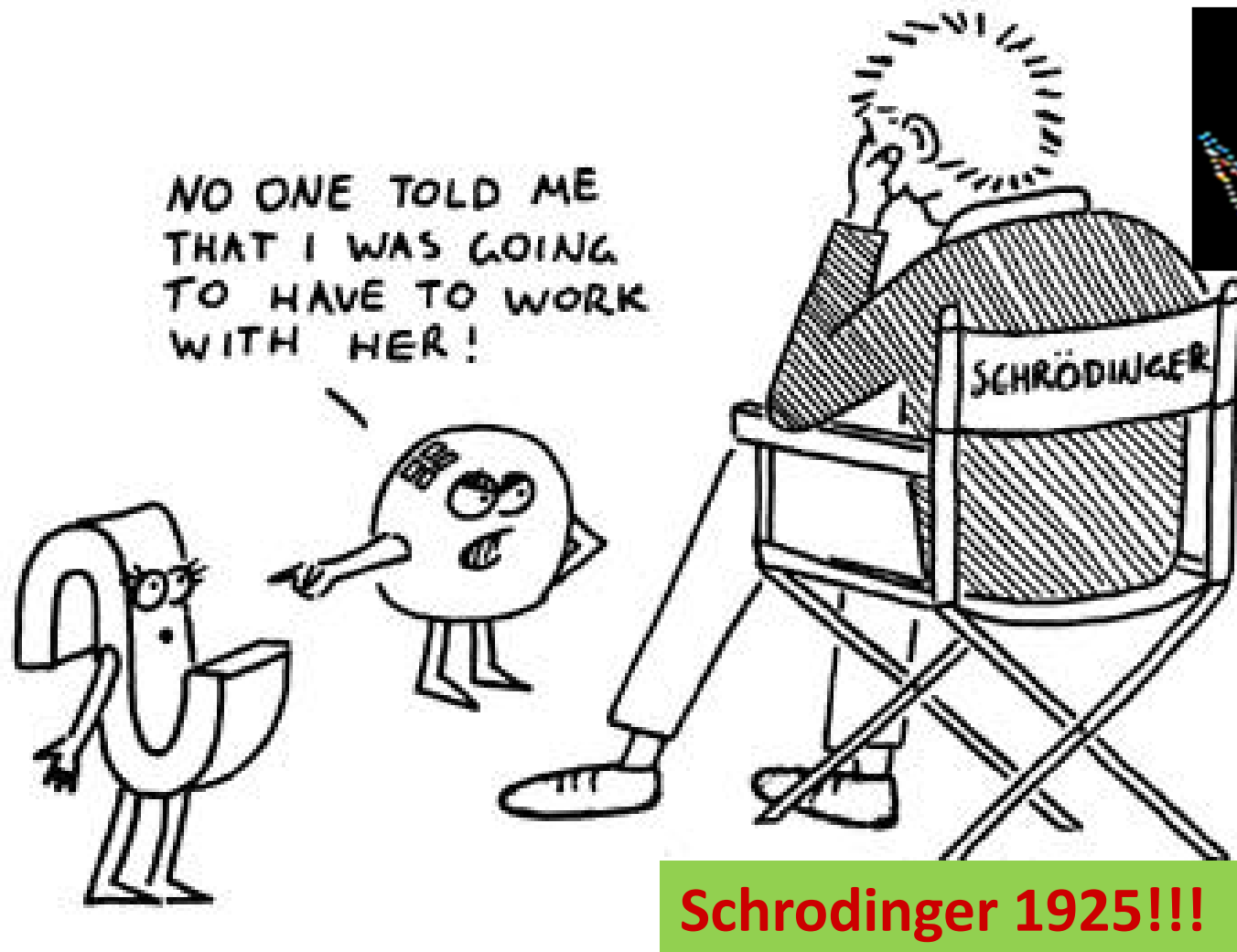
Light can have "particle-like" and "wave-like" properties; Matter (electrons & atoms) have "particle-like" and "wave-like" properties, but we do not know what they really are!!

A handwritten word "Wave!" in black ink. The letters are stylized and slightly slanted. The exclamation mark is drawn with a series of vertical squiggles.

When we refer to a (QM) particle,
What we really mean is a "wave-particle"

Why do we need a new theory for dynamics of electrons, atoms or molecules

- Wavelike equation for describing sub/atomic systems
- *Probabilistic, not deterministic (non-newtonian)*



Schrodinger 1925!!!

Can we derive Schrödinger Equation?

3-1 *The Schrödinger Equation Is the Equation for the Wave Function of a Particle*

We cannot derive the Schrödinger equation anymore than we can derive Newton's laws, and Newton's second law, $f = ma$, in particular. (We shall regard the Schrödinger equation to be a fundamental postulate, or axiom of quantum mechanics, just as Newton's laws are fundamental postulates of classical mechanics.) (Even though we cannot derive the Schrödinger equation, we can at least show that it is plausible and perhaps even trace Schrödinger's original line of thought. We finished Chapter 1 with a discussion of matter

$$H\psi = E\psi$$

“We **CANNOT** derive Schrodinger equation anymore than we can derive Newton's laws”

What do we mean by Wavefunction Ψ ?

- In quantum mechanics, **wavefunction** of a particle is a mathematical entity that contains all the dynamical information about the system.
- It contains where the particle can be found, its linear momentum, any property of the system that you ask about.
- It is the central carrier of information in quantum mechanics

What is a Hamiltonian Operator?

Operator is a mathematical object which acts on a function to give a new function

$$x \sin(Ax) = x \sin(Ax)$$

operator function New function

"x" here is an operator for position

Operator for Energy: Hamiltonian

$$E_{\text{tot}} = T + V.$$

The operator for the kinetic energy along x-axis is

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2},$$

The potential energy is a function of position

$$\hat{V} = V(x).$$

What are Eigenfunctions and Eigenvalues?

Eigenfunctions are a special set of functions which have the property that, when they are acted upon by a particular operator, they are unchanged, apart from being multiplied by a constant

The constant obtained is called eigenvalue

$$\hat{A} \phi = \lambda \times \phi.$$

$$\frac{d}{dx} \phi(x) = \lambda \phi(x).$$

$$E_{\text{tot}} = T + V.$$

$$\begin{aligned} \frac{d}{dx} \phi(x) &= \frac{d}{dx} [B \exp(Cx)] \\ &= CB \exp(Cx) \\ &= C\phi(x). \end{aligned}$$

What can't we solve the Schrödinger of H-atom in Cartesian Coordinates?

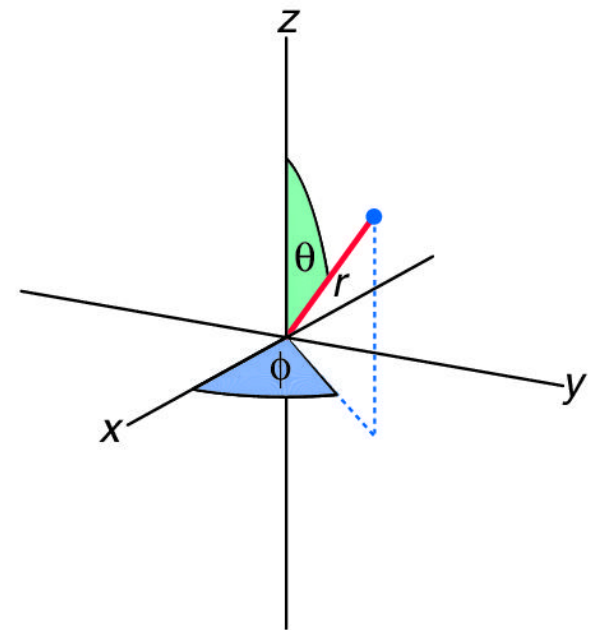
$$\hat{H}\psi(x, y, z) = E \cdot \psi(x, y, z) \quad \text{Eigen Value}$$

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

Road-Block: This 2nd order PDE with **3 variables...**
Can not be separated!!!

Hamiltonian: Spherical Polar Coordinates

x	$=$	r	\sin	θ	\cos	ϕ
y	$=$	r	\sin	θ	\sin	ϕ
z	$=$	r	\cos	θ		



Completely solvable problem!!!

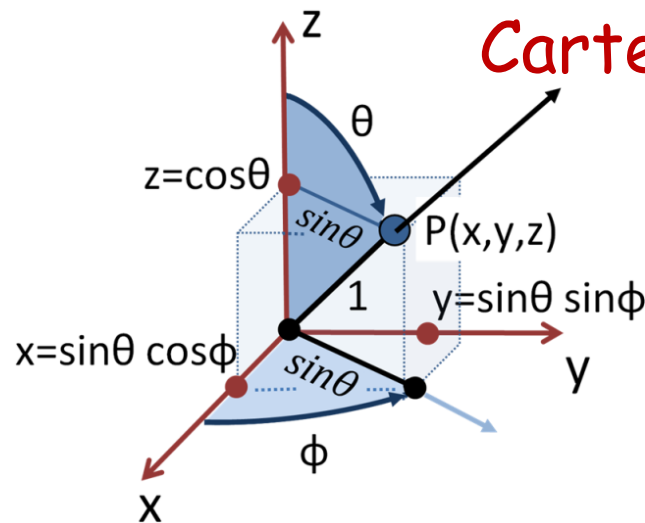
What are Spherical Polar Coordinates?



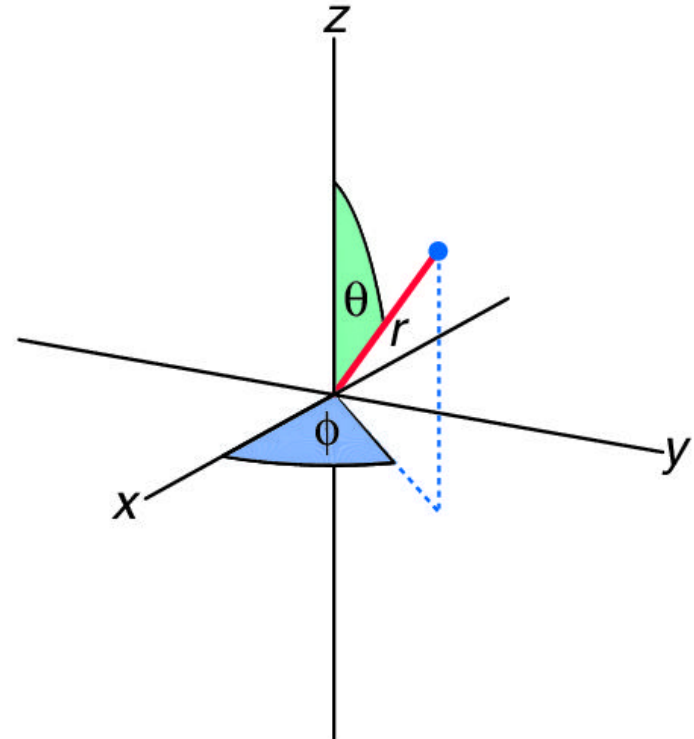
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- 'r' ranges from 0 to ∞
- the co-latitude θ ranges from 0 (north pole) to π (south pole)
- the azimuth ϕ ranges from 0 to 2π

Conversion from
Cartesian coordinates ?



$$\begin{aligned}x &= r \sin \theta \cos \phi \\y &= r \sin \theta \sin \phi \\z &= r \cos \theta\end{aligned}$$



What we learnt from solving SE?

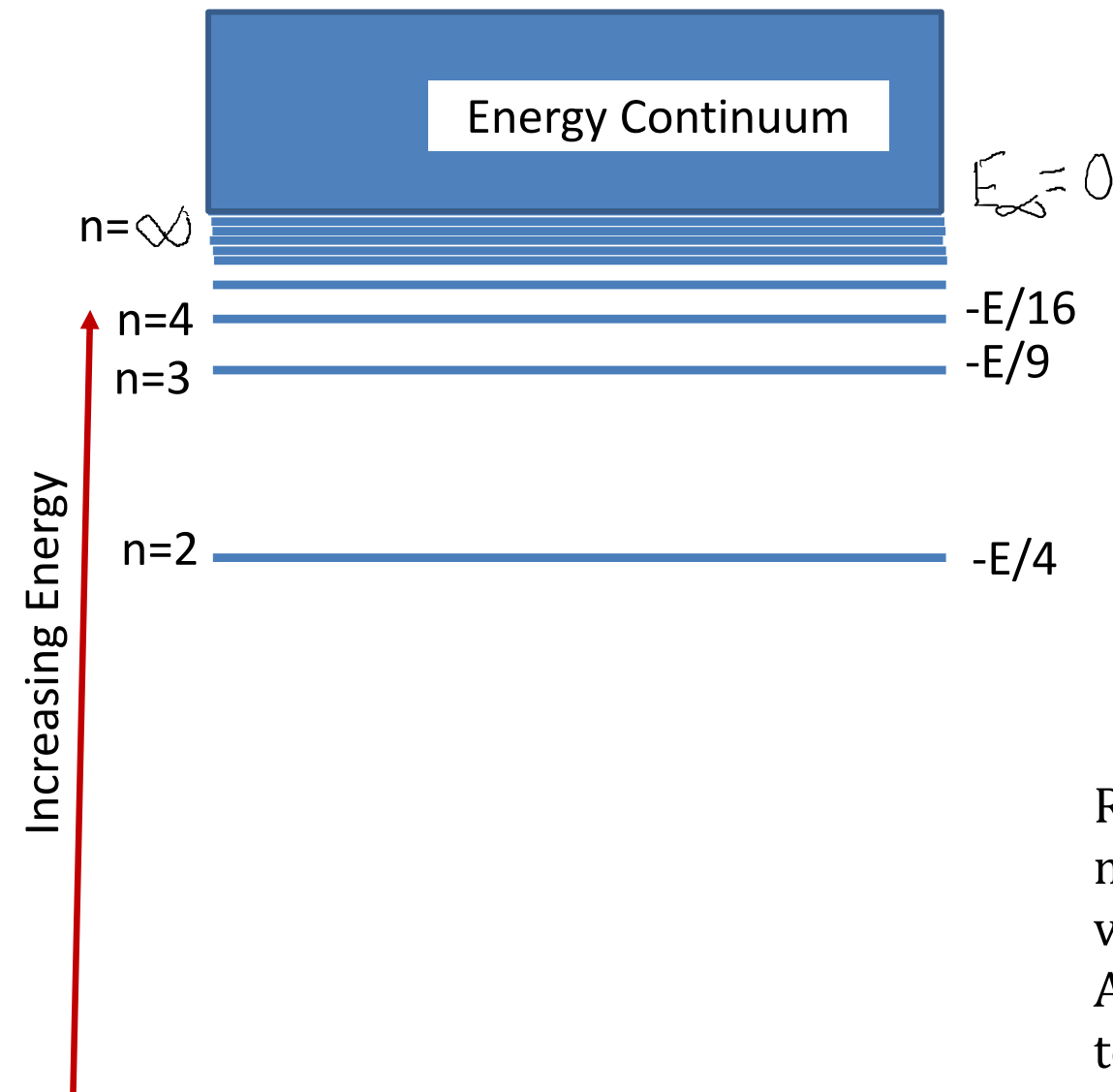
Formulate a correct Hamiltonian
(total energy) Operator H

Solve $H\Psi = E\Psi$ (2nd order PDE)
by separation of variable and
intelligent trial/guess solutions

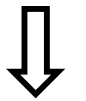
**Probability and
Average Values**

Energies of states
Corresponding to
Quantum Numbers

Quantum Numbers
that specify the
"state" of the system



$$E = -\frac{1}{n^2} \frac{me^4}{8\epsilon_0^2 h^2}$$



$$E = -\frac{R_h}{n^2}$$

R_h is Rydberg Constant = $2.17987 \times 10^{-18} \text{ J}$
 n = principal quantum numbers; allowed values $1, 2, 3, \dots, \infty$
 Allowed energies are often written in terms of n

$n=1$ _____ $-E = R_h$

For energies of H-like atoms such as He^+ :

$$E = -\frac{Z^2 R_h}{n^2}$$

Define $\Psi (r, \theta, \phi, t)$?

- Ψ in general is a function of r, θ, ϕ and t denoted as $\Psi (r, \theta, \phi, t)$
- We will look at wave functions which are called stationary waves, i.e. Ψ which are not dependent on t - in those cases we are looking a Ψ when the atom is stable and sitting idle
- The Ψ we will look at will be $\Psi (r, \theta, \phi)$ also known as time-independent QM
- When we go and solve Schrodinger equation for $\Psi (r, \theta, \phi)$, two more quantum number drop out in the differential equation.

l : The angular Quantum Number

- We get a new quantum no l , called the angular momentum quantum number because
- It dictates how much angular momentum the electron has
- It also has allowed values- $0, 1, 2, \dots, (n-1)$
- Classically thinking l would denote the angular momentum

m : Magnetic Quantum Number

- The third quantum number which drops out is m , called the magnetic quantum number
- It dictates how an atom moves/behaves in a magnetic field
- More precisely what m is the z -component of the angular momentum
- Allowed values of m are $m=0, \pm 1, \pm 2, \dots, \pm l$

Is Ψ_{nlm} = Orbitals????

- For $n=1$, $l=0$, $m=0$, the electron is called to be in 100 state and the wave function corresponding to this electron is Ψ_{100}
- The other wave functions possible for $n=2$ are Ψ_{200} , Ψ_{210} , Ψ_{211} and Ψ_{21-1}
- All these four states have the same energy i.e. $-R_H/4$
- The other way of representing the wave function is a orbital...the orbital is actually the wave-function
- If $l=0$, s; $l=1$, p; $l=2$, d
- So all Ψ_{210} , Ψ_{211} and Ψ_{21-1} would be called 2p.

What does Ψ_{nlm} mean?

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

TABLE 2.1 Hydrogenlike Wavefunctions* (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions			(b) Angular wavefunctions		
n	l	$R_{nl}(r)$	l	" m_l " [†]	$Y_{lm_l}(\theta, \phi)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	1	x	$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi$
2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	1	y	$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \sin \phi$
3	0	$\frac{2}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} \left(3 - \frac{2Zr}{a_0} + \frac{2Z^2r^2}{9a_0^2}\right) e^{-Zr/3a_0}$	1	z	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
3	1	$\frac{2}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{3a_0}\right) e^{-Zr/3a_0}$	2	xy	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \sin 2\phi$
3	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$	2	yz	$\left(\frac{15}{4\pi}\right)^{1/2} \cos \theta \sin \theta \sin \phi$
			2	zx	$\left(\frac{15}{4\pi}\right)^{1/2} \cos \theta \sin \theta \cos \phi$
			2	$x^2 - y^2$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \cos 2\phi$
			2	z^2	$\left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$

*Note: In each case, $a_0 = \epsilon_0 h^2 / \pi m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.

[†]In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l .

What does $\Psi^2_{nlm}(r,\theta,\varphi)$ mean?

- What does the wave function actually mean and how does it actually represent the electron?
- Wave function is just a mathematical function

Max Born: If I take the wave function and I square it, if I interpret that as a probability density then I can interpret all the predictions made in the Schrodinger equation

$$\Psi^2_{nlm}(r,\theta,\varphi) = \text{probability density or probability/unit volume}$$

H-Atom Complete $\Psi(r,\theta,\phi)$ for $n=1,2$

1s $n=1$ $l=0$ $m=0$ $\psi_{100} =$

$e^{-\sigma} = \psi_{1s}$

$\sigma \rightarrow r/a_0$

F(r) only

2s $n=2$ $l=0$ $m=0$ $\psi_{200} =$

$(2 - \sigma)e^{-\sigma/2} = \psi_{2s}$ **F(r) only**

2p_z $l=1$ $m=0$ $\psi_{210} =$

$\sigma e^{-\sigma/2} \cos \theta = \psi_{2p_z}$ **F(r, θ)**

2p_{x,y} $l=1$ $m=\pm 1$ $\psi_{21\pm 1} =$

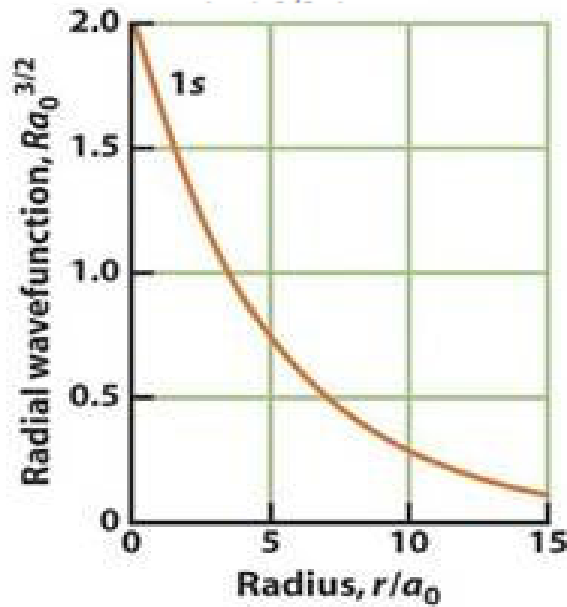
$\sigma e^{-\sigma/2} \sin \theta e^{\pm i\phi} = \psi_{2p_{x,y}}$ **F(r, θ , ϕ)**

S-Orbitals ($l=0, m_l=0$)" R_{n1} and R_{n1}^2

$$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

$$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$



S-Orbitals ($l=0, m_l=0$)" R_{nl} and R_{nl}^2

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$$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

