Chemical Engineering 412

Introductory Nuclear Engineering

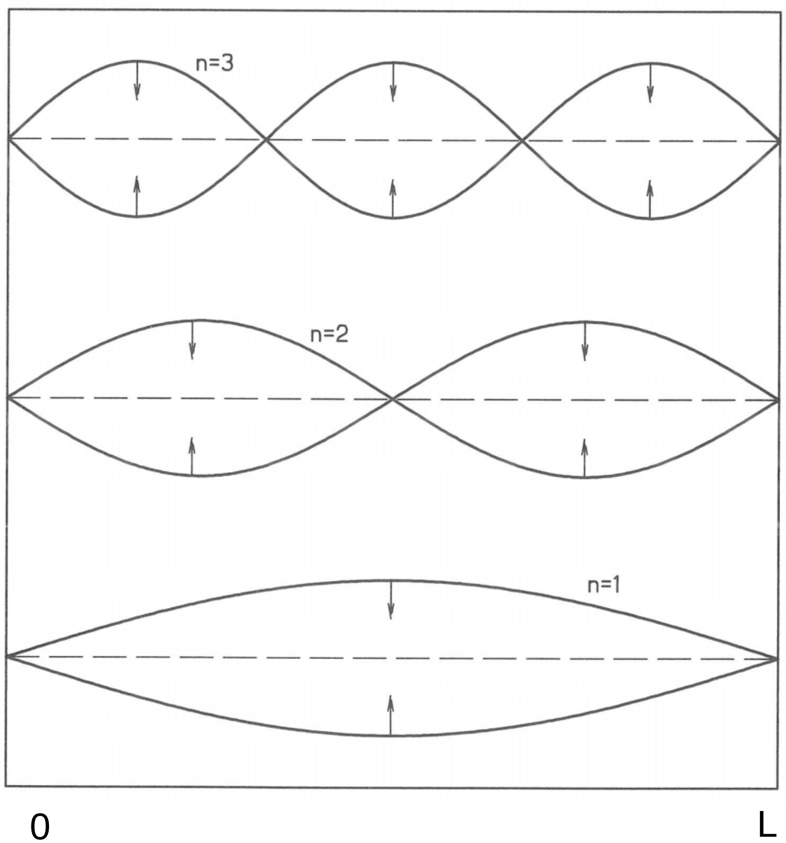
Lecture 3

Quantum Mechanics II

Schrödinger's Wave equation

Schrödinger's Wave equation

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{1}{u^2}\frac{\partial^2 \Psi(x,t)}{\partial t^2}$$



$$\Psi(0,t) = \Psi(L,t) = 0$$

$Note: Solution\ is\ separable\ in\ x\ and\ t$

Also, $t_c = \frac{1}{v}, \frac{n\pi u t_c}{L} = 2\pi$

$$\Psi(x,t) = A\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi u t}{L}\right) \quad n = 1, 2, 3, \dots$$

Wave Equation Solution

$$v = \frac{nu}{2L}, \qquad \mathrm{u} = \lambda v$$

$$\Psi(x,t) = \psi(x)T(t)$$

$$\Psi(x,t) = \psi(x)\sin(2\pi v t) \quad n = 1, 2, 3, \ldots$$

Plug this expression into the wave equation:

$$\frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2 v^2}{u^2}\psi(x) = 0 \text{ or } \frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0$$

$$\nabla^2\psi(x,y,z) + \frac{4\pi^2}{\lambda^2}\psi(x,y,z) = 0$$

Apply to bound electron (only one)

- Assume:
  - Nucleus produces electric field on electron, V(x, y, z)
  - Electron has rest mass m (=m_o)
  - Electron kinetic energy = T
  - Electron total energy = E
  - Electron potential energy = V
  - *T=E-V;* $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mT}} = \frac{h}{\sqrt{2m(E-V)}}$

$$-\frac{h^2}{8\pi^2 m}\nabla^2\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$$

Observations on Results

- Only two possible solutions
  1. $\psi(x, y, z)$=0 (trivial)
  2. If E has discrete values; E=E_n, n=0,1,2,3…
     - E_n is eigenvalue, $\psi_n(x, y, z)$ is Eigenfunction
- I.E. electron can only have discrete energy levels – verified
- ψ_n is called a "wave function"
  - Complex quantity, extends over all space
  - Relative amplitude of the particle wave
  - If ψ_n' is a solution, so is ψ_n=ψ_n'A
  - A is selected so that $\iiint \psi_n(x, y, z)\psi_n^*(x, y, z)dV = 1$

Quantum Mechanics

- Particle energy exists in discrete quantities.
- Changes occur over discrete intervals.
- Responsible for maintaining atomic structure (classical model would decay rapidly).
- Electron energy states described by orbitals and are statistical rather than deterministic. These are described by quantum states or numbers.
- Schrödinger's wave equation describes energy levels

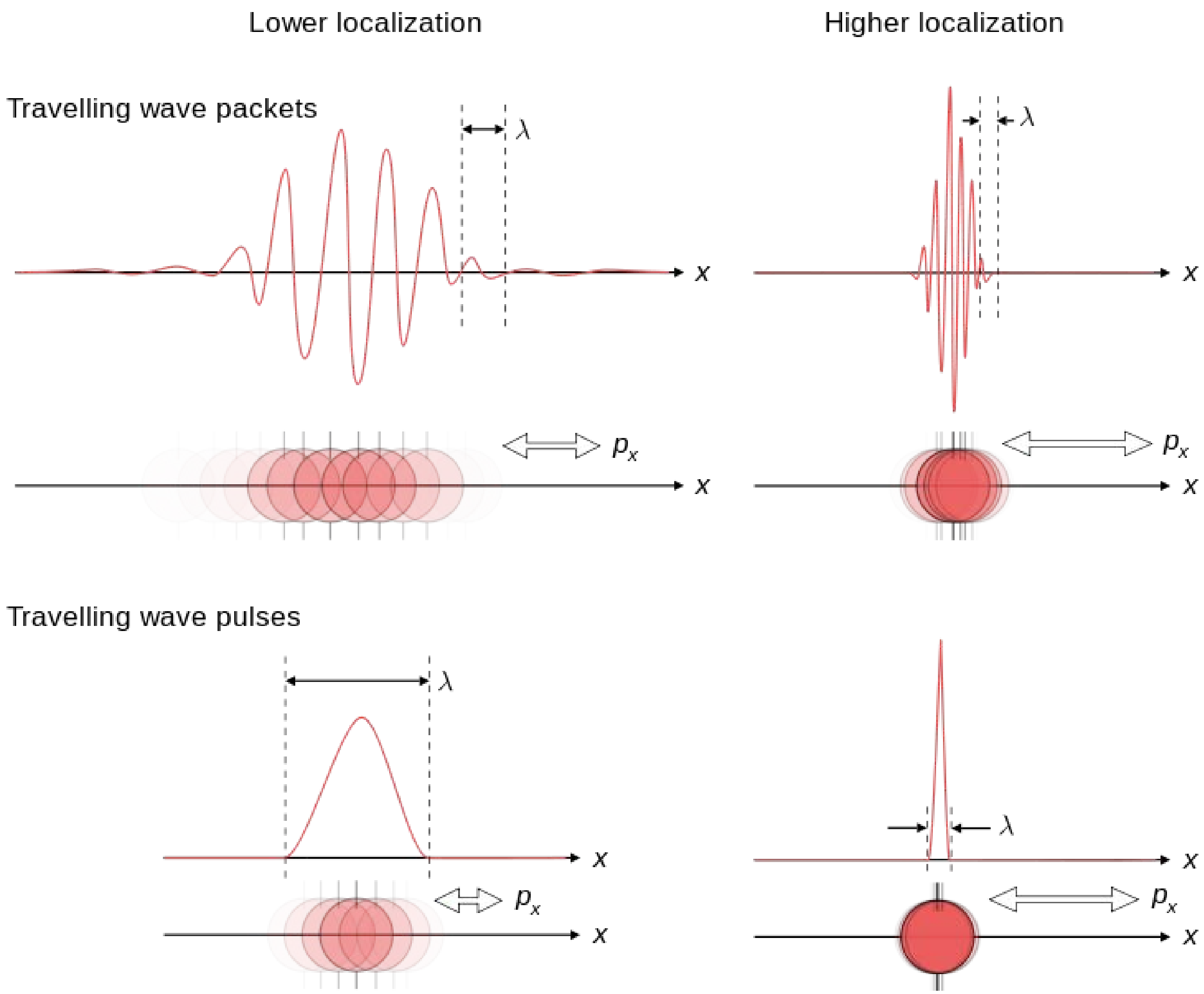
$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + V(\vec{r})\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)$$

$$\hbar = \frac{h}{2\pi}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$$

steady-state

Particle-wave Duality



Uncertainty Principle

$$\Delta x \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2} \qquad \Delta t \Delta E \geq \frac{h}{4\pi} = \frac{\hbar}{2}$$

- Position and momentum are fundamentally linked
  - Cannot determine both with arbitrary accuracy.
- Analogously, energy and time are linked
  - Energy of Particle
  - Time a particle remains in a given energy state

Quantum Mechanics (cont'd)

- Quantum particles can penetrate energy barriers that would normally be impenetrable in classical mechanics.
- There is inherent uncertainty in pairs of properties for quantum particles.
  - momentum-position
  - energy-time

Particle in a 1D Box

- Assume:
  - Zero potential in Box, Infinite Potential Outside
  - $\psi(x)$= 0 at x=0 and x=a
  - $\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 mE}{h^2}\psi(x) = 0$
  - $\mathrm{k} = \frac{8\pi^2 mE}{h^2}$

$$\psi(x) = Asin(kx) + Bcos(kx)$$

$$\psi(x) = 0 = Asin(0) + Bcos(0) = B$$

$$\psi(x) = 0 = Asin(ka)$$

$$k = \frac{n\pi}{a}, n = 1, 2, 3\ldots; \;\; \psi(x) = Asin\left(\frac{n\pi x}{a}\right)$$

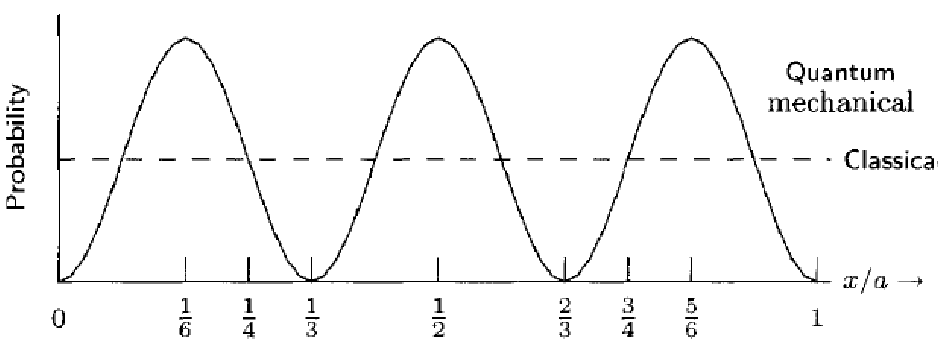
Particle in a 1D Box (continued)

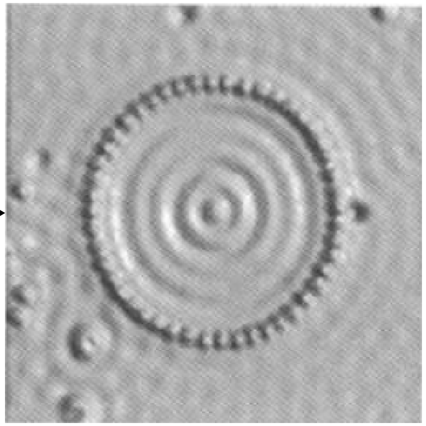
- $E = \frac{h^2 k_n}{8\pi^2 m} = \frac{h^2 n^2}{8ma^2}$

$$\int_0^a |\psi_n(x)|^2 \, dx = A \int_0^a sin\left(\frac{n\pi x}{a}\right) dx = 1$$

$$\psi(x) = \sqrt{\frac{2}{a}} sin \frac{n\pi x}{a}, n = 0,1,2,3 \ldots$$

$$|\psi(x)|^2 dx = \frac{2}{a} sin^2 \frac{n\pi x}{a} dx$$





Hydrogen atom electron

- Fully 3D (spherical) model a.k.a. box
- $V(r) = -e^2/r$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}\left[E-V(r)\right]\psi=0,$$

$$\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$$

$$\frac{d^2\Phi(\phi)}{d\phi^2}=-m^2\Phi(\phi).$$

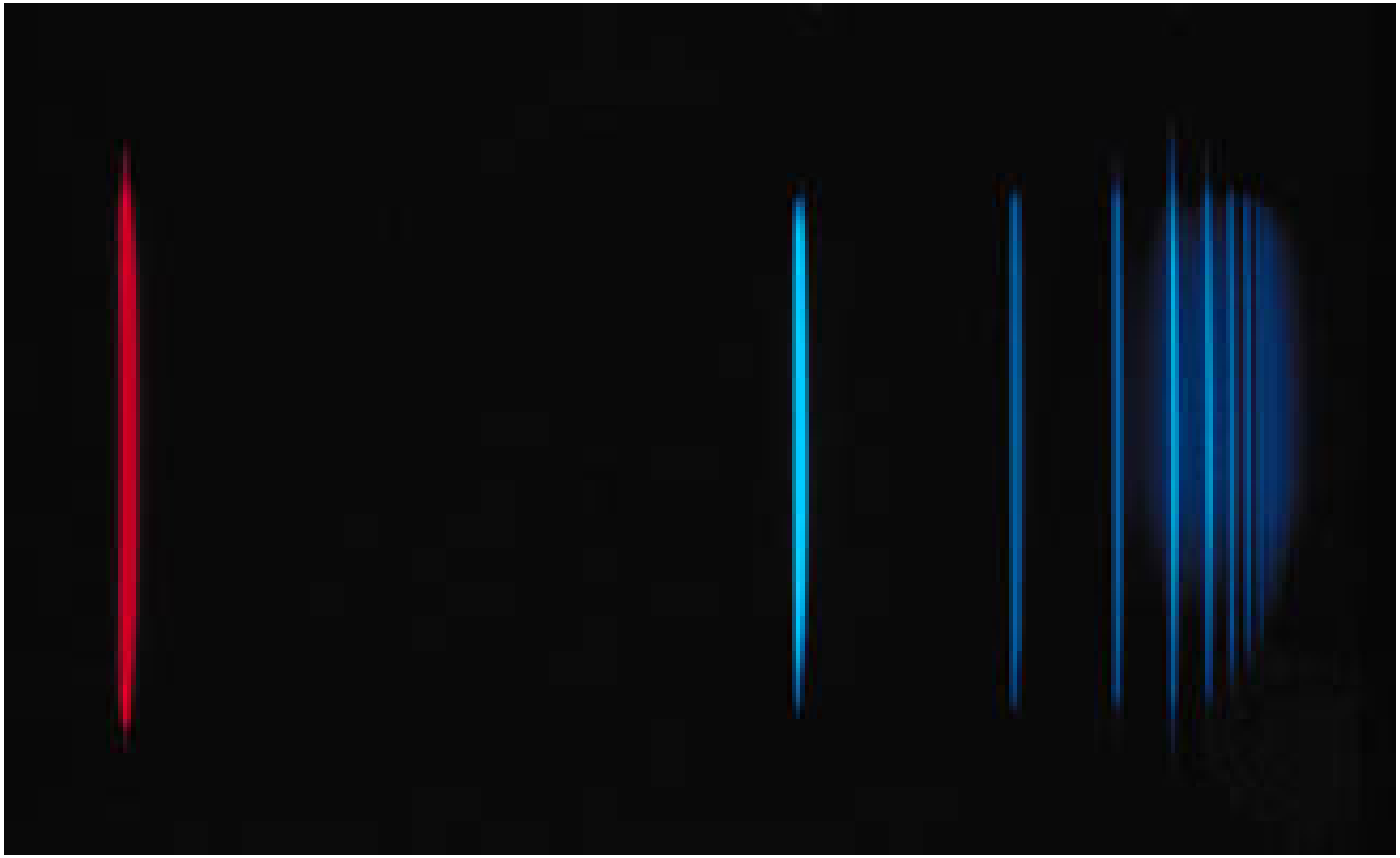
$$\frac{1}{\sin\theta}\frac{d^2\Theta(\theta)}{d\theta^2}-\frac{m^2}{\sin^2\theta}\Theta(\theta)+\beta\Theta(\theta)=0$$

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right]+-\frac{\beta}{r^2}R(r)+\frac{8\pi^2\mu}{h^2}\left[E-V(r)\right]R(r)=0$$

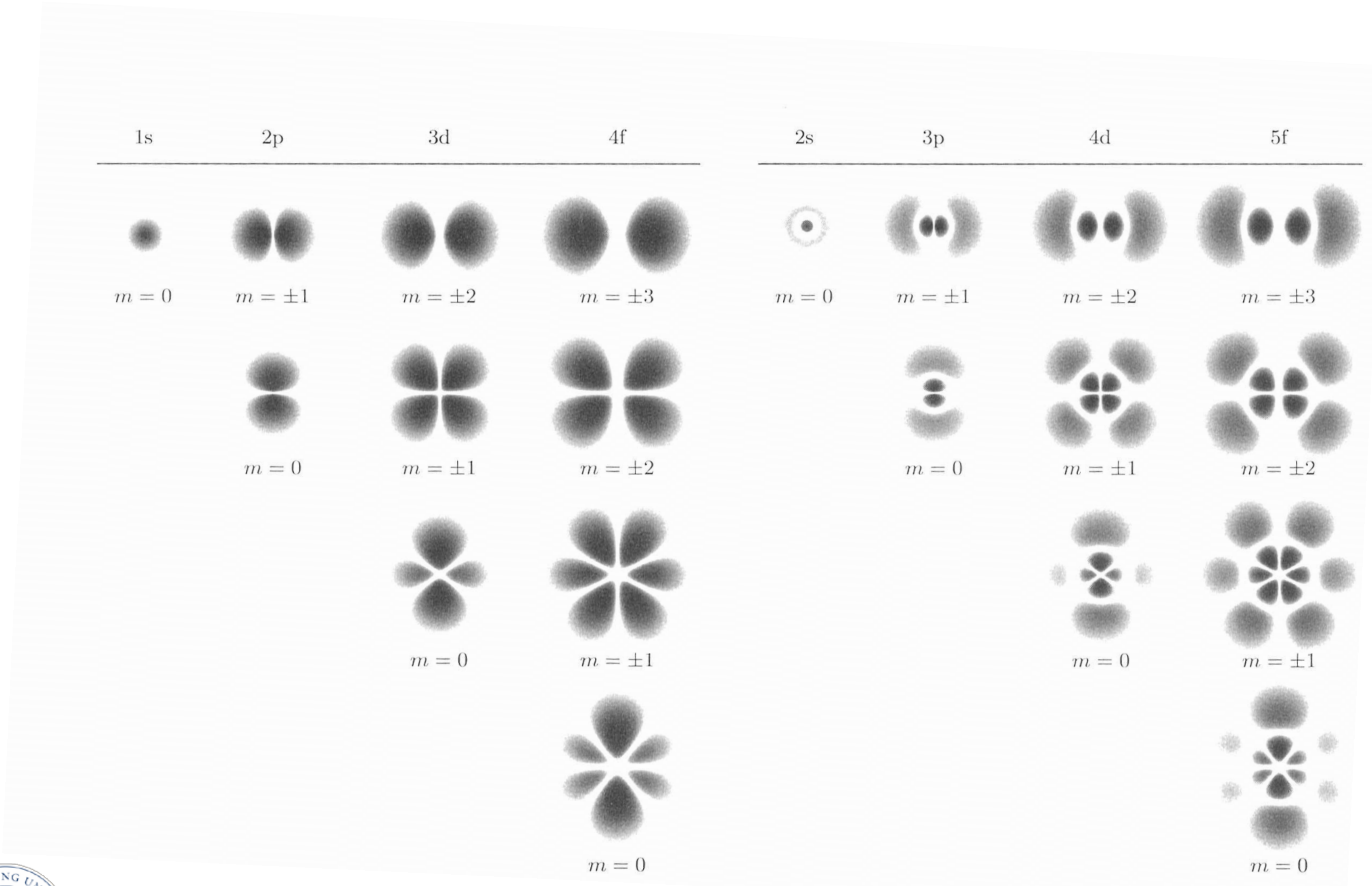
Hydrogen Solution

- Solution to $\frac{d^2\Phi(\phi)}{d\phi^2} = -m^2\Phi(\phi).$
  - $\Phi(\phi) = Asin(m\phi) + Bcos(m\phi)$
  - Solutions only exist if:
    - m, l, and n are constrained
    - m is integer, m = 0,$\pm$1 ,$\pm$2 ,$\pm$3… - azmuthal
    - β = l(l+1) – angular momentum
    - $E_n = \frac{2\pi^2\mu e^2}{h^2n^2}, n = 1, 2, 3$ – principal
- These define electron clouds!
  - m has 2l+1 values
  - l can't be greater than n-1
  - m_s = $\pm$1/2 – added if S.E. is relativistically evaluated

Balmer series from hydrogen

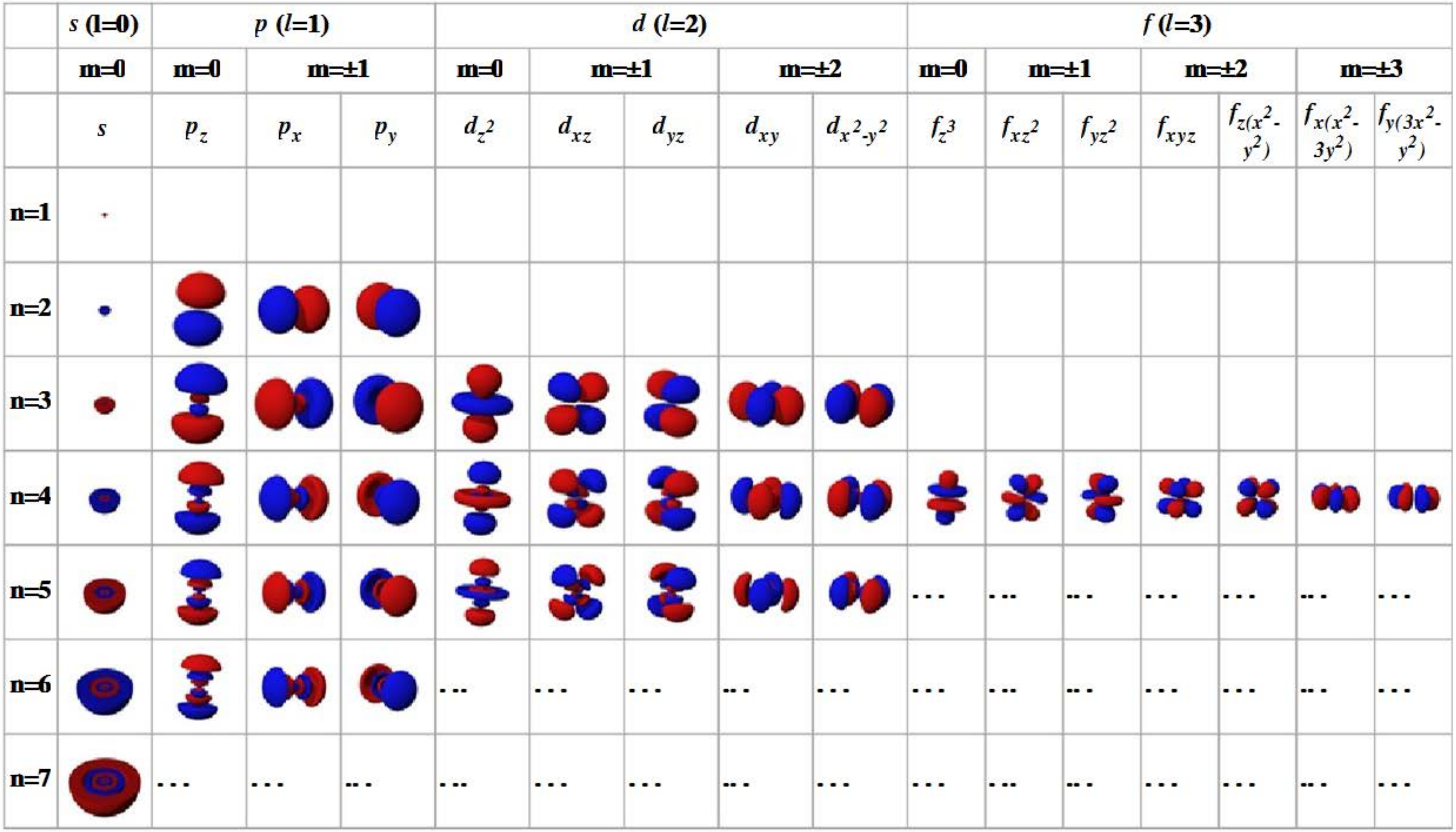


Hydrogen Electron Density Maps



...views of the probability density in a pl...

Orbital Shapes



	s (l=0)	p (l=1)			d (l=2)					f (l=3)						
	m=0	m=0	m=±1		m=0	m=±1		m=±2		m=0	m=±1		m=±2		m=±3	
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	f_{z^3}	f_{xz^2}	f_{yz^2}	f_{xyz}	$f_{z(x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{y(3x^2-y^2)}$
n=1																
n=2																
n=3																
n=4																
n=5										...	...	...	...	...	...	...
n=6					...	...	...	...	...	...	...	...	...	...	...	...
n=7		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...

Periodic Table