

Chemical Engineering 412

Introductory Nuclear Engineering

Lecture 3

Quantum Mechanics II

Schrödinger's Wave equation



Schrödinger's Wave equation

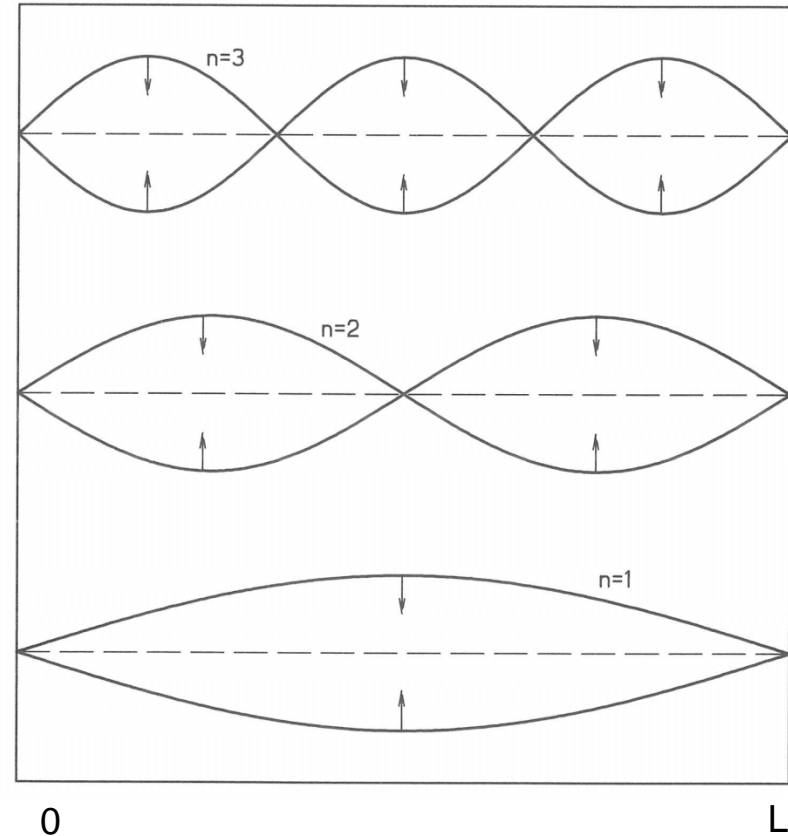
$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = \frac{1}{u^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2}$$

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

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

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

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

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

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
 - $T=E-V$; $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mT}} = \frac{h}{\sqrt{2m(E - V)}}$

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



Observations on Results

- Only two possible solutions
 1. $\psi(x, y, z)=0$ (trivial)
 2. If E has discrete values; $E=E_n$, $n=0,1,2,3\dots$
 - 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 $\psi_n=\psi_n'A$
 - 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

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

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

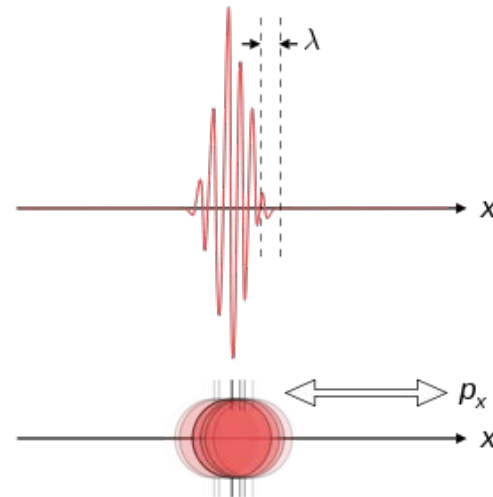
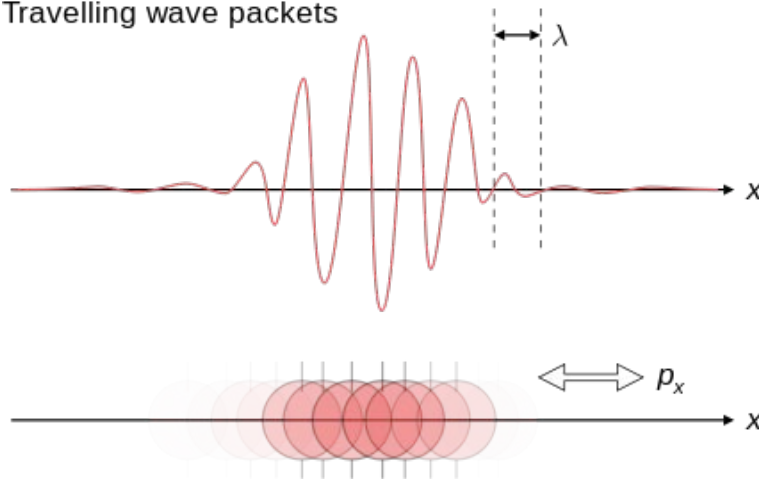


Particle-wave Duality

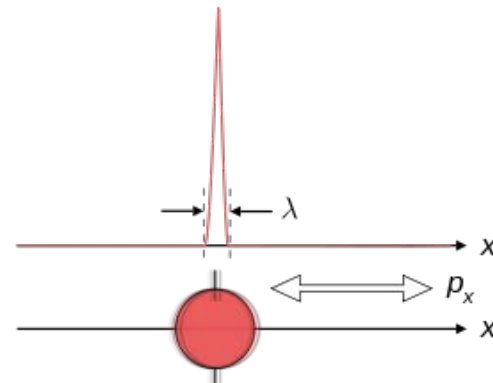
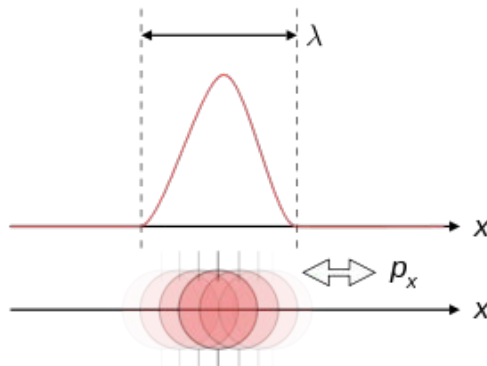
Lower localization

Higher localization

Travelling wave packets



Travelling wave pulses



Uncertainty Principle

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

- 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 $x=a$
 - $\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2mE}{h^2}\psi(x) = 0$
 - $k = \frac{8\pi^2mE}{h^2}$

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

$$\psi(x) = 0 = A\sin(0) + B\cos(0) = B$$

$$\psi(x) = 0 = A\sin(ka)$$

$$k = \frac{n\pi}{a}, n = 1, 2, 3 \dots; \quad \psi(x) = A\sin\left(\frac{n\pi x}{a}\right)$$



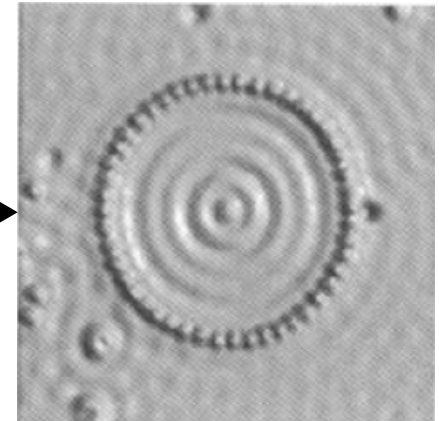
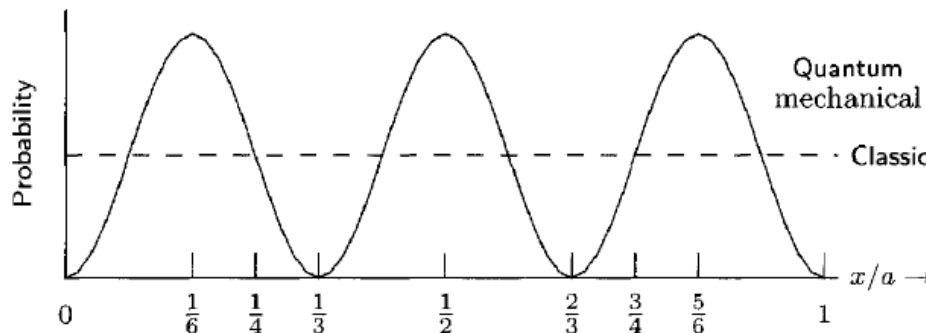
Particle in a 1D Box (continued)

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

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

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

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



Hydrogen atom electron

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

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

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

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

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

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

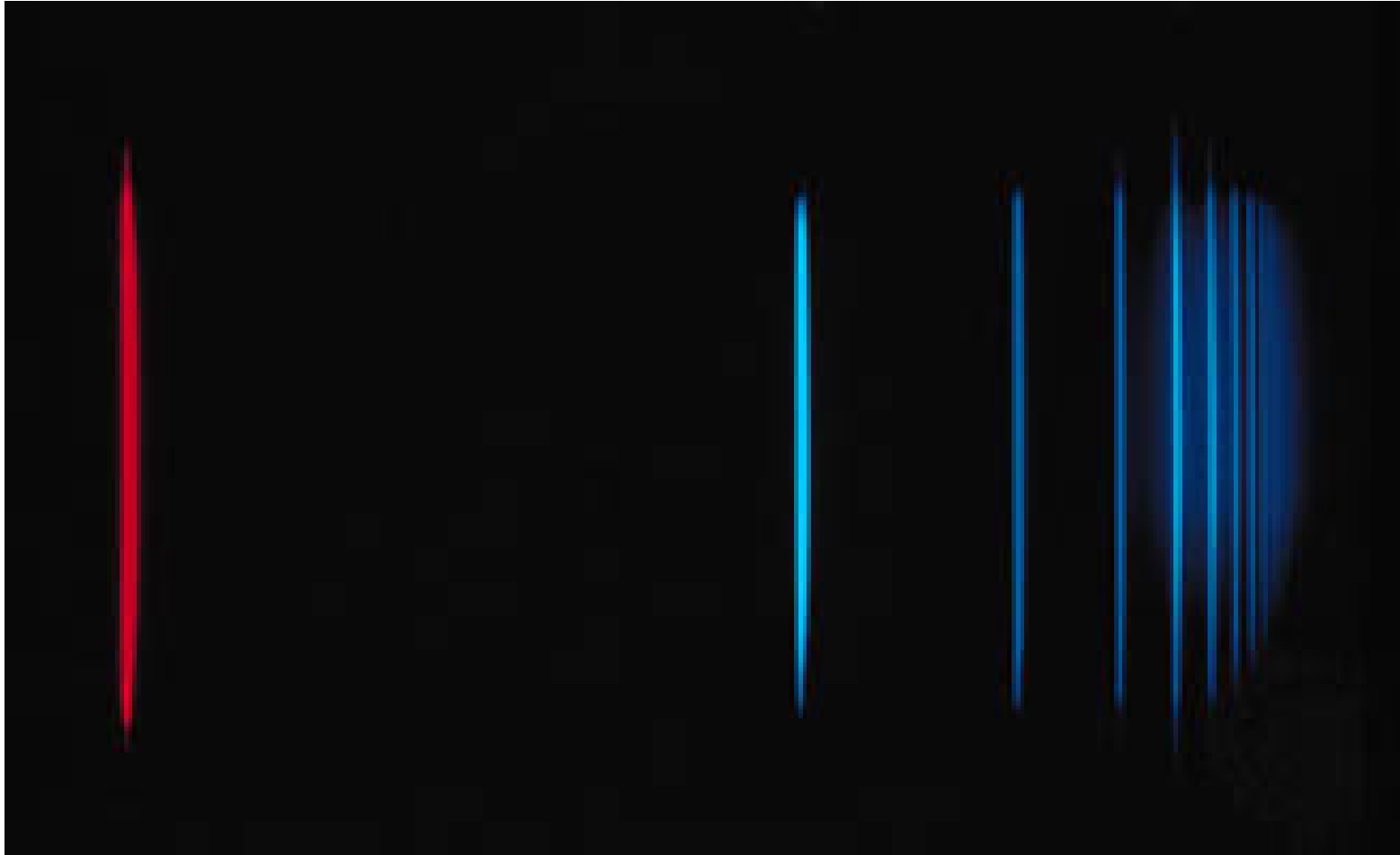


Hydrogen Solution

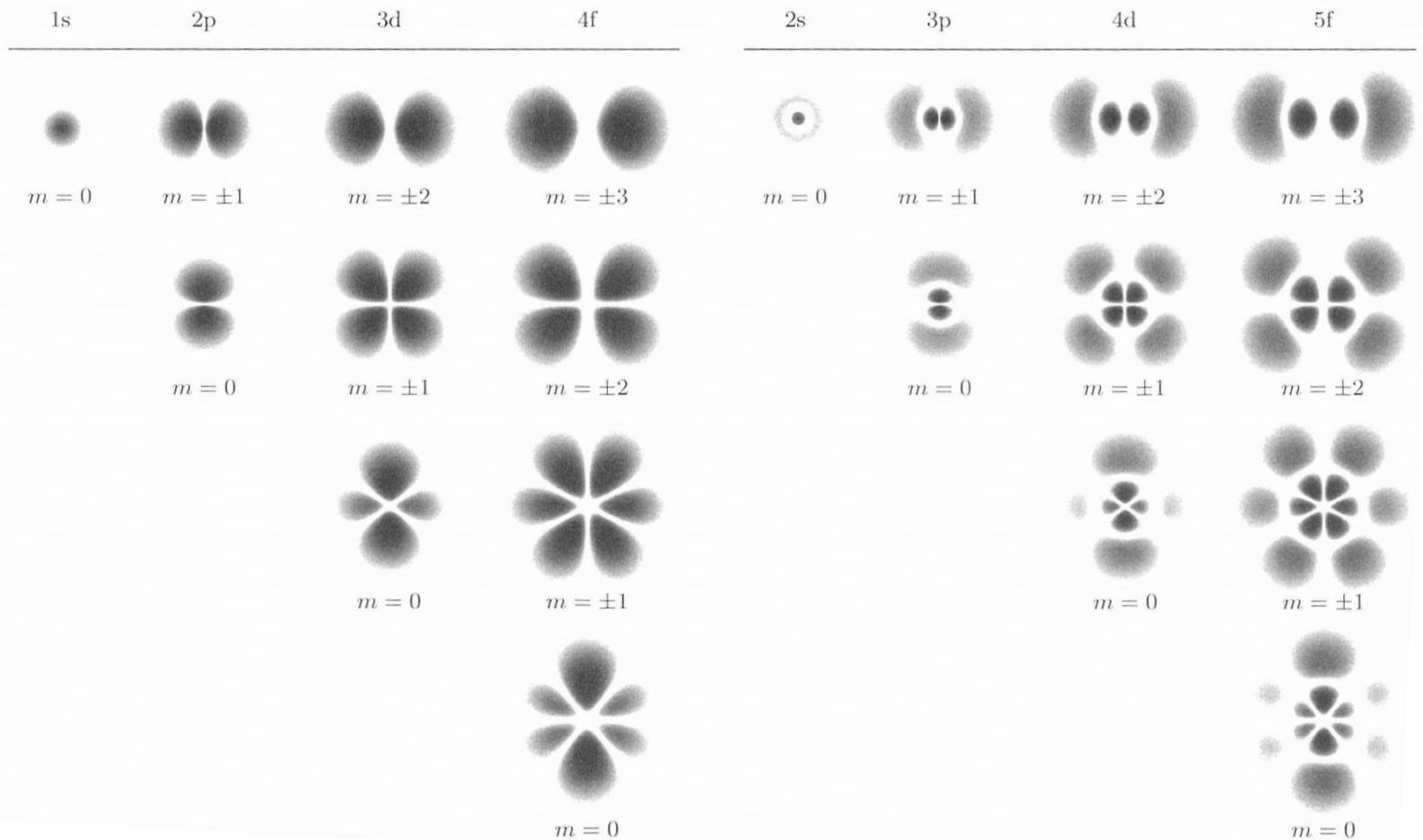
- Solution to $\frac{d^2\Phi(\phi)}{d\phi^2} = -m^2\Phi(\phi)$.
 - $\Phi(\phi) = A\sin(m\phi) + B\cos(m\phi)$
 - Solutions only exist if:
 - m, l , and n are constrained
 - m is integer, $m = 0, \pm 1, \pm 2, \pm 3, \dots$ - azimuthal
 - $\beta = l(l+1)$ – angular momentum
 - $E_n = \frac{2\pi^2\mu e^2}{h^2 n^2}, n = 1, 2, 3$ – 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



Classical views of the probability density in a pl

Orbital Shapes

	$s (l=0)$	$p (l=1)$			$d (l=2)$					$f (l=3)$						
	$m=0$	$m=0$	$m=\pm 1$		$m=0$	$m=\pm 1$		$m=\pm 2$		$m=0$	$m=\pm 1$		$m=\pm 2$		$m=\pm 3$	
	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

Periodic Table of Elements

1A	1	H	2	He	0
2	3	Li	4	Be	
3	11	Na	12	Mg	
4	19	K	20	Ca	
5	37	Rb	38	Sr	
6	55	Cs	56	Ba	
7	87	Fr	88	Ra	
	21	Sc	22	Ti	
	23	V	24	Cr	
	25	Mn	26	Fe	
	27	Co	28	Ni	
	29	Cu	30	Zn	
	31	Ga	32	Ge	
	33	As	34	Se	
	35	Br	36	Kr	
	37	Rb	38	Sr	
	39	Y	40	Zr	
	41	Nb	42	Mo	
	43	Tc	44	Ru	
	45	Rh	46	Pd	
	47	Ag	48	Cd	
	49	In	50	Sn	
	51	Sb	52	Te	
	53	I	54	Xe	
	55	Cs	56	Ba	
	57	*La	58	Ce	
	59	Pr	60	Nd	
	61	Pm	62	Sm	
	63	Eu	64	Gd	
	65	Tb	66	Dy	
	67	Ho	68	Er	
	69	Tm	70	Yb	
	71	Lu			
	72	Hf	73	Ta	
	74	W	75	Re	
	76	Os	77	Ir	
	78	Pt	79	Au	
	80	Hg	81	Tl	
	82	Pb	83	Bi	
	84	Po	85	At	
	86	Rn			
	87	Fr	88	Ra	
	89	+Ac	90	Th	
	91	Pa	92	U	
	93	Np	94	Pu	
	95	Am	96	Cm	
	97	Bk	98	Cf	
	99	Es	100	Fm	
	101	Md	102	No	
	103	Lr			

* Lanthanide Series

+ Actinide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Legend - click to find out more...

H - gas

Li - solid

Br - liquid

Tc - syn

Non-Metals

Transition Metals

Rare Earth Metals

Halogens

Alkali Metals

Alkali Earth Metals

Other Metals

Inert Elements

