Quantum Mechanics

Some relations from classical mechanics

$$KE = \frac{1}{2}mv^2 \quad \& \quad p = mv \quad \Rightarrow \quad KE = \frac{p^2}{2m}$$

$$E = KE + PE \quad \text{or} \quad E = \frac{p^2}{2m} + V(x)$$

In quantum mechanics

Define "wave function" for electron $\psi(x)$

$|\psi(x)|^2$ **= probability electron of finding electron at x**

momentum

$p \rightarrow$ **operator on** $\psi(x)$

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

$$\boxed{p\psi = -i\hbar\frac{d\psi}{dx} \qquad p\psi = -i\hbar\frac{\Delta\psi}{\Delta x}}$$

not required

$$p^2\psi = -\hbar^2\frac{d^2\psi}{dx^2}$$

Schrödinger Equation for $\psi(x)$

(must include "boundary conditions" on ψ !!!)

$$E\psi = \frac{p^2}{2m}\psi + V(x)\psi$$

solve this equation for stationary states (standing waves)

for $\psi(x)$ **&** **for the allowed E (energy) values**

Well beyond scope of course

Note: we have left out time dependence of Schrödinger Eqn.

$$i\hbar\frac{d\psi}{dt} = \frac{p^2}{2m}\psi + V(x)\psi$$

we assumed

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

$$\psi(x,t) = e^{-i\frac{E}{\hbar}t}\psi(x)$$

Which reduces to

$$E\psi(x) = \frac{p^2}{2m}\psi(x) + V(x)\psi(x)$$

For the stationary space dependent Schrödinger Equation

probability electron of finding electron at x

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$$|\psi(x,t)|^2 = \left|e^{-i\frac{E}{\hbar}t}\psi(x)\right|^2 = \left|e^{-i\frac{E}{\hbar}t}\right|^2 |\psi(x)|^2 = 1|\psi(x)|^2$$

Aside on solution of differential equation

Schrödinger Equation for free particle

$$\frac{p^2}{2m}\ \psi(x) = E\ \psi(x)$$

$$\frac{p^2}{2m}\ \psi - E\psi = 0$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - E\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \left[\frac{2mE}{\hbar^2}\right]\psi = 0$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} = \frac{2\pi}{\lambda}$$

$$\frac{d^2\psi}{dx^2} + \left[k^2\right]\psi = 0$$

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

Newton's Equation for harmonic oscillator

$$F = ma = -kx$$

$$ma + kx = 0$$

$$a + \left[\frac{k}{m}\right]x = 0$$

$$\frac{d^2x}{dt^2} + \left[\frac{k}{m}\right]x = 0 \qquad \omega = \sqrt{\frac{k}{m}}$$

$$\frac{d^2x}{dt^2} + \omega^2\ x = 0$$

$$x(t) = A\sin(\omega t) + B\cos(\omega t)$$

or $x(t) = A\sin(\omega t + \delta)$

Aside on solution of differential equation

Spring: Simple Harmonic – x – v – a – check of motion eq.

$$\boxed{\mathbf{x = A\sin(\omega t+\delta)} \quad \text{or} \quad x = A\sin(\omega t) + B\cos(\omega t)}$$

$$\mathbf{v = \frac{dx}{dt} = A\frac{d[\sin(\omega t+\delta)]}{dt} = A\,\omega\cos(\omega t+\delta)}$$

$$\mathbf{v = A\,\omega\cos(\omega t+\delta)}$$

$$\mathbf{a = \frac{dv}{dt} = A\omega\frac{d[\cos(\omega t+\delta)]}{dt} = -A\,\omega^2\sin(\omega t+\delta)}$$

$$\mathbf{a = -A\,\omega^2\sin(\omega t+\delta)}$$

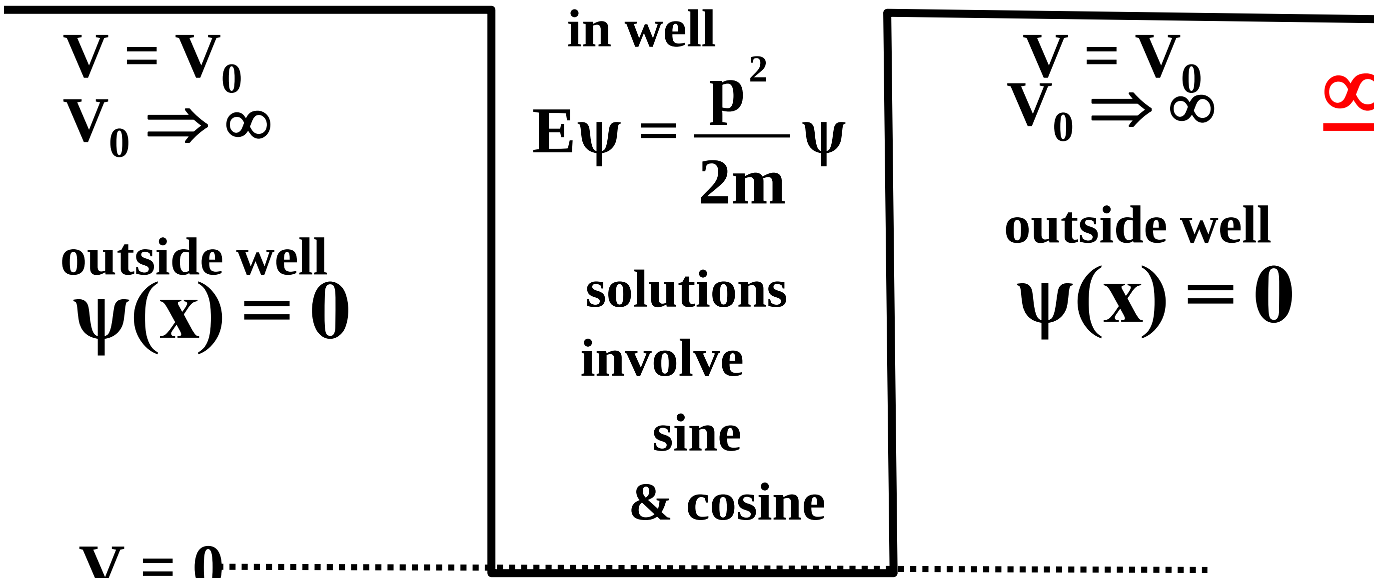
$$\mathbf{a+\omega^2 x = 0} \qquad \mathbf{\frac{d^2x}{dt^2}+\omega^2 x = 0}$$

$$\mathbf{-A\,\omega^2\sin(\omega t+\delta)+\omega^2 A\sin(\omega t+\delta) = 0}$$

$$\mathbf{-A\,\omega^2\sin(\omega t+\delta)+\omega^2 A\sin(\omega t+\delta) = 0}$$

∞ Square Well

just like standing waves on string problem !!!



$\psi(x) = 0$

$\psi(x = 0) = 0$ $\quad$ $\psi(x = L) = 0$

This equation (and it's solutions) are identical to standing waves on A string that we considerer earlier in course !!

1.) in well wave function ψ has a sine or cosine form

2.) wave function ψ must go to 0 at well ends $\{\psi(x=0) = \psi(x=L) = 0\}$

3.) wave function ψ must be 0 outside

inside & outside ψ match at x=0 & L

$x = 0$

$\psi(x=0)=0$

$x = L$

$\psi(x=L)=0$

phase factor (where you choose x=0)

$$\boxed{\psi(x)=\psi_0\ \sin\left(2\pi\frac{x}{\lambda}+\varphi\right)}$$

wave length

$$0 = \psi_0\ \sin(\varphi)$$

$$\boxed{0=\varphi}$$

$$0=\psi_0\ \sin\left(2\pi\frac{L}{\lambda}\right)$$

$$2\pi\frac{L}{\lambda}=\pi,2\pi,3\pi,\ldots n\pi$$

wave function sin form

+ boundary conditions !!!!

$$\boxed{L=n\frac{\lambda}{2}\qquad n=1,2,3,\ldots}$$

$\Rightarrow$ **full solution**

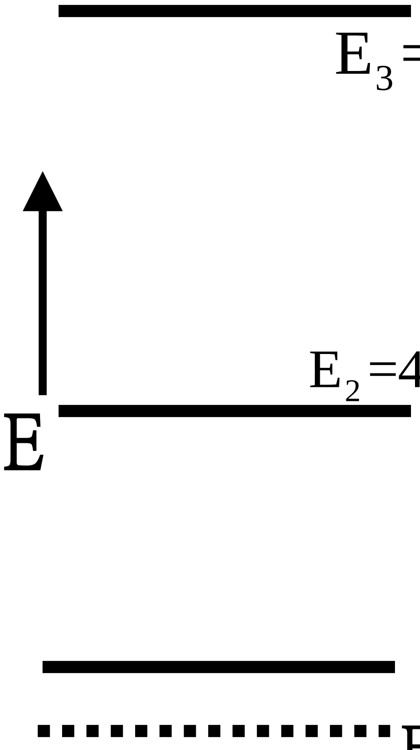
$$\boxed{\psi(x)=\psi_0\ \sin\left(\pi n\frac{x}{L}\right)}$$

$$L = n\frac{\lambda}{2} \qquad n=1,2,3,\ldots \qquad \Rightarrow \qquad |p| = \frac{h}{\lambda} = \frac{h}{2L/n} = \frac{nh}{2L}$$

$$\Rightarrow \qquad E_n = \frac{p^2}{2m} = \frac{1}{2m}\left(\frac{nh}{2L}\right)^2 = n^2\left[\frac{1}{8m}\left(\frac{h}{L}\right)^2\right] \qquad n=1,2,3,\ldots$$

note

$$E_n = n^2\left[E_1\right] \qquad n=1,2,3,\ldots$$



$E_3 = 9E_1$

E

$$E_2 = 4E_1 = \frac{1}{2m}\left(\frac{h}{L}\right)^2$$

$$E_1 = \frac{1}{8m}\left(\frac{h}{L}\right)^2$$

$E = 0$

note: for lowest n=1 state

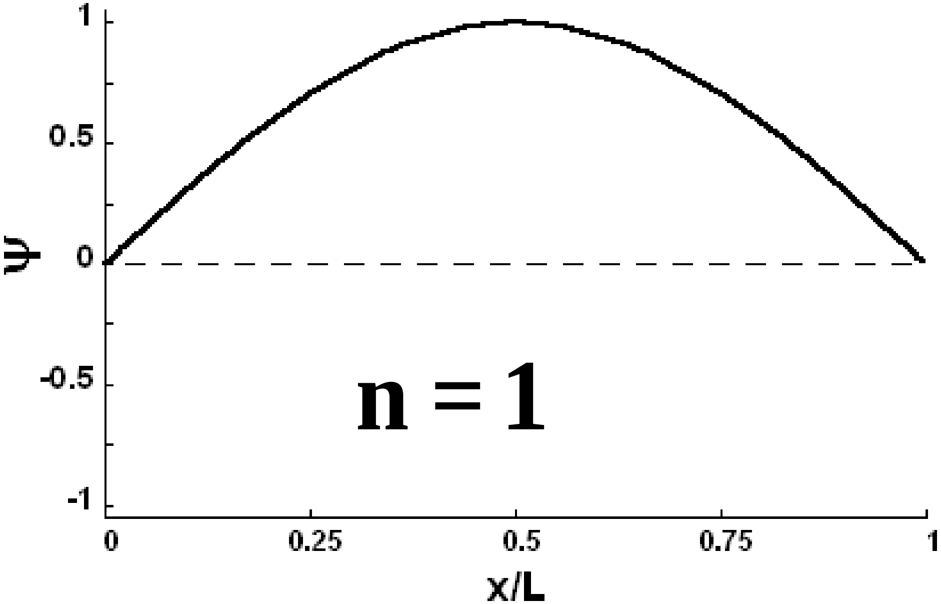
$$E_1 = \frac{1}{8m}\left(\frac{h}{L}\right)^2 \qquad |p_1| = \frac{h}{2L}$$

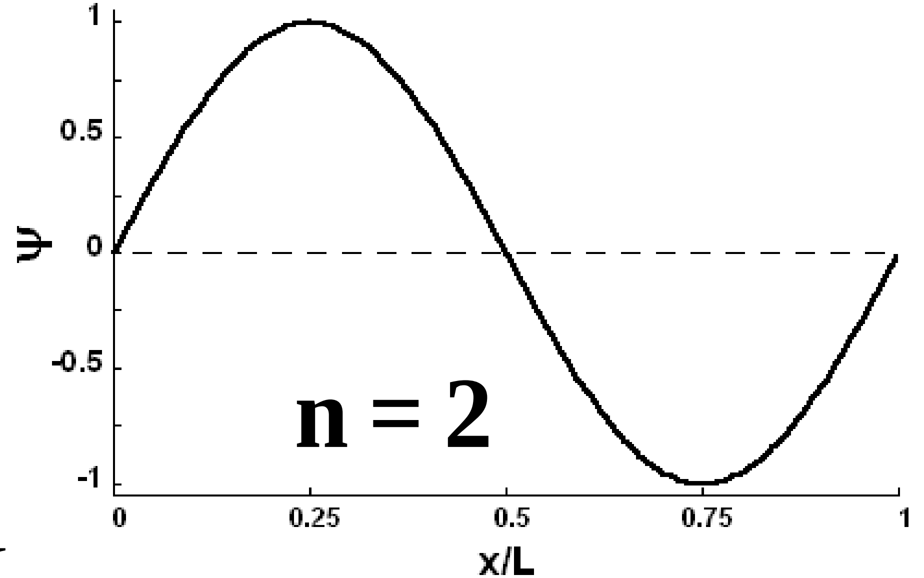
finite momentum magnitude= motion)

Like standing wave on string, standing wave constructed from left + right traveling waves i.e. +p and -p

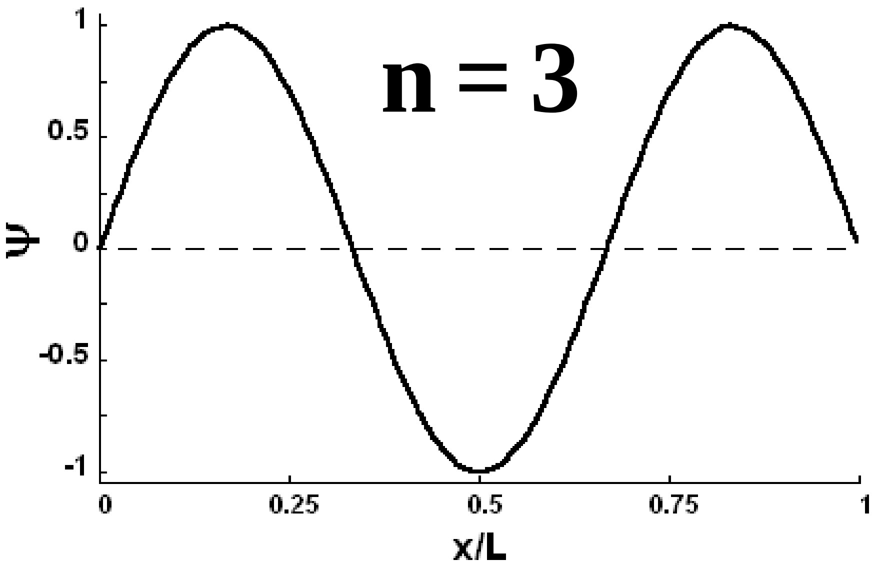
http://phet.colorado.edu/en/simulation/bound-states

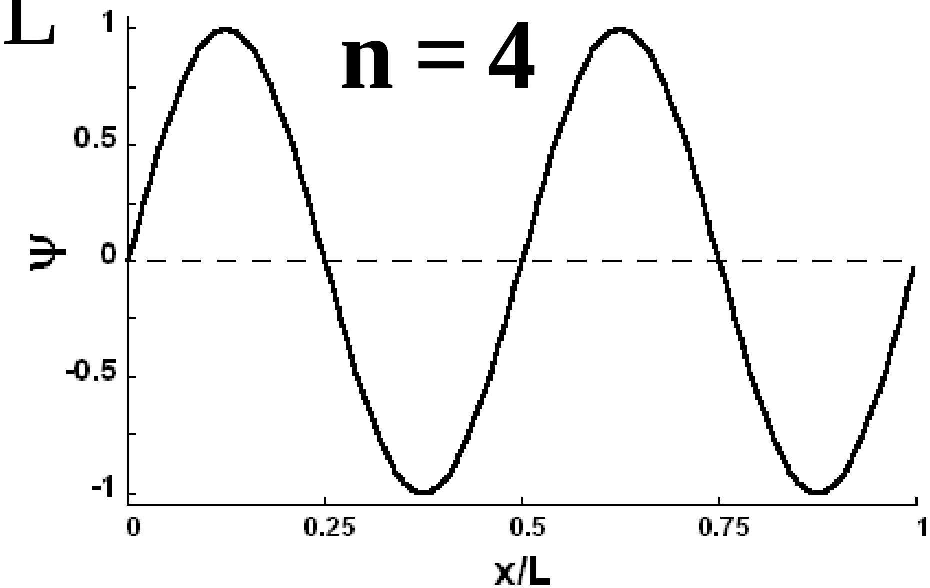
n=1-4 wave functions for ∞ square well





$$\psi_n(x) = \sin\left(n\pi \frac{x}{L}\right)$$

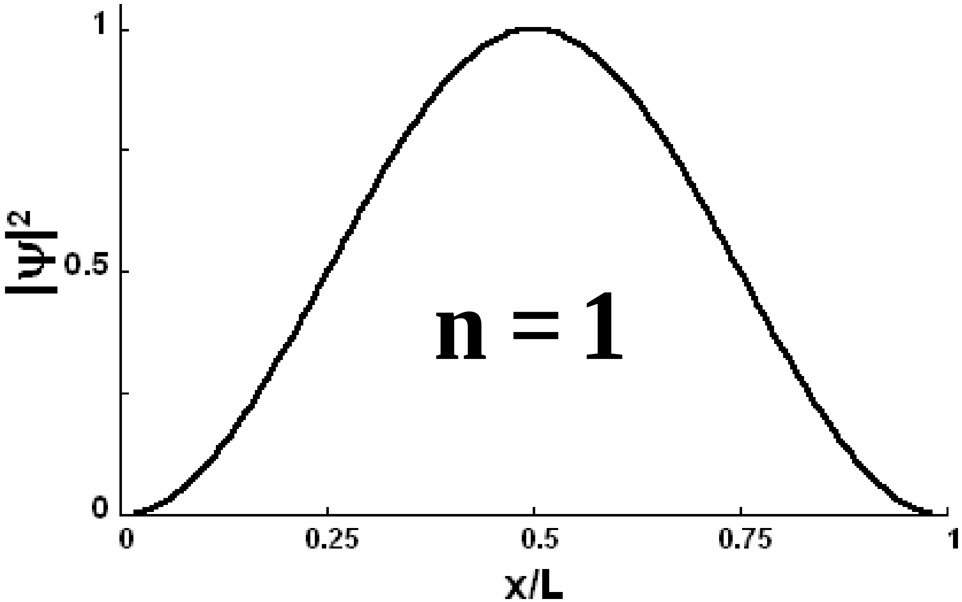


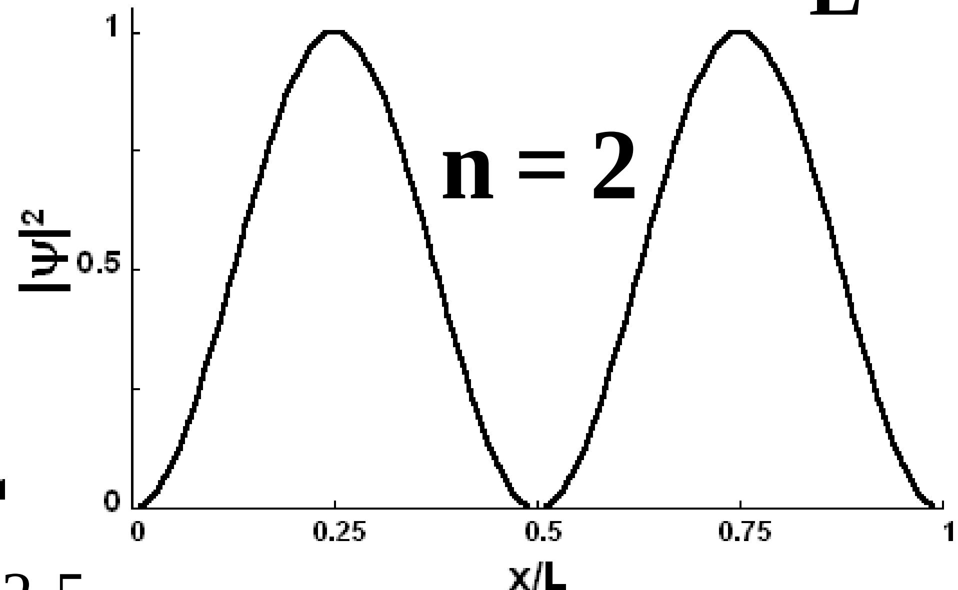


n=1-4 probability for ∞ square well

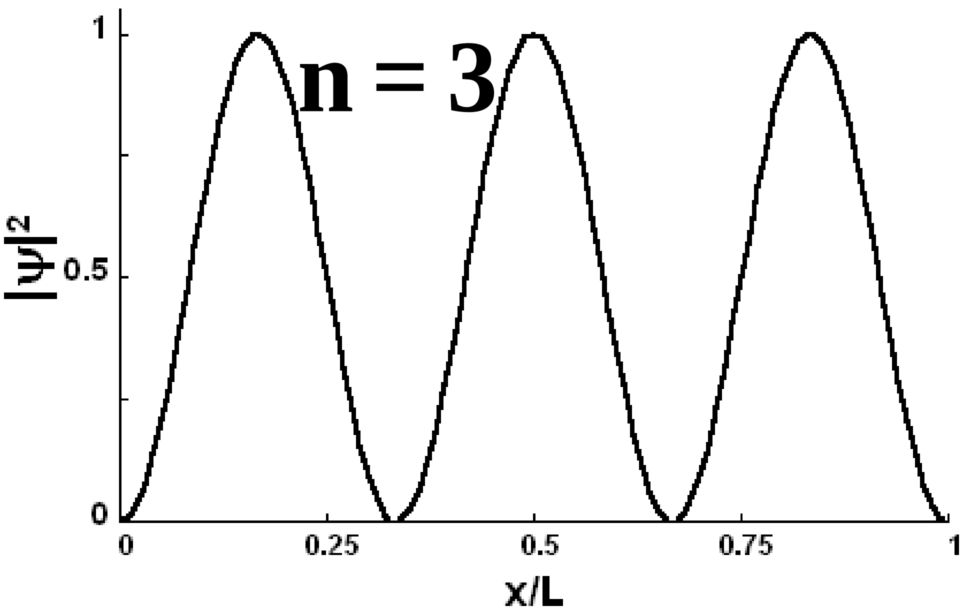
12-4.1

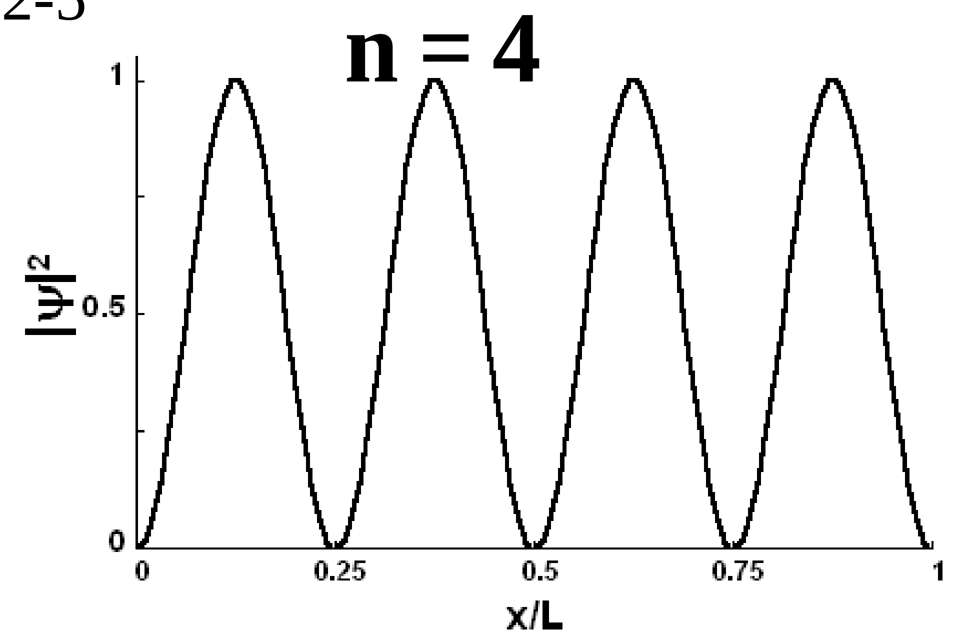
$$\left|\psi_n(x)\right|^2 = [\sin(n\pi \frac{x}{L})]^2$$





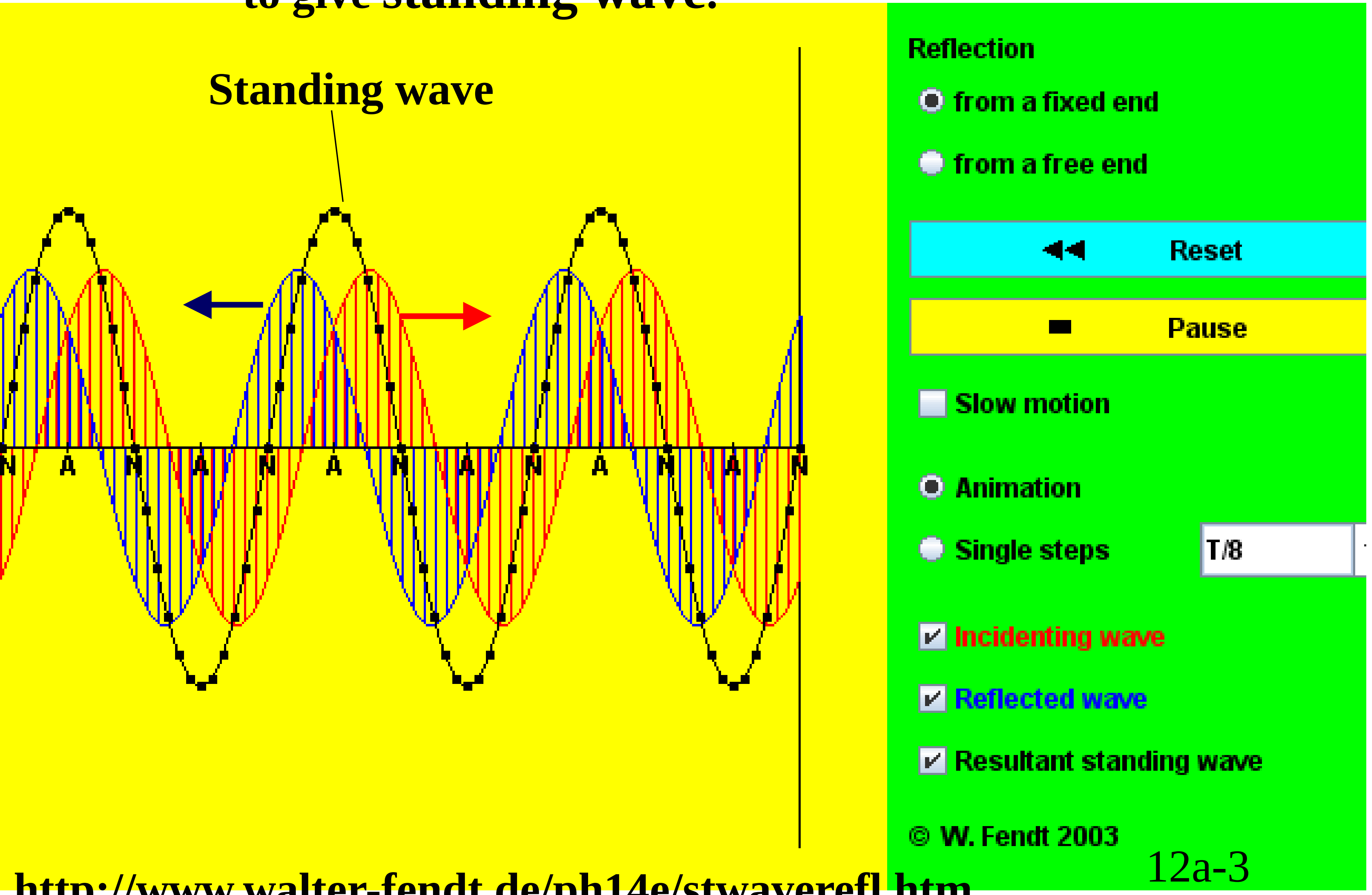
12-5





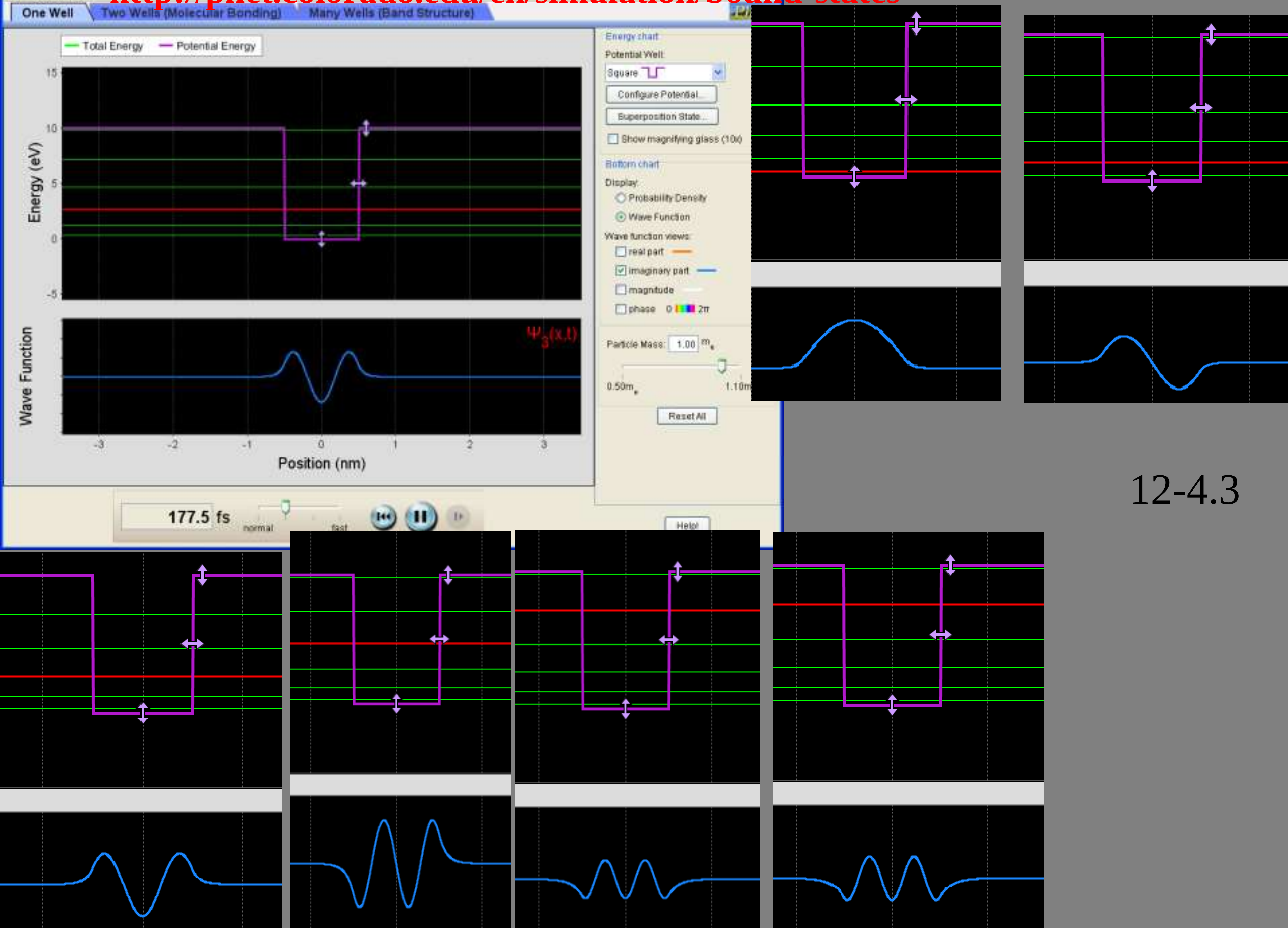
recall

Interference of right and left traveling waves to give standing wave.



http://www.walter-fendt.de/ph14e/stwaverefl.htm

http://phet.colorado.edu/en/simulation/bound-states



12-4.3

Uncertainty Principle

$$\underbrace{\Delta p\,\Delta x \gtrsim \hbar}_{1} : \underbrace{\Delta E\,\Delta t \gtrsim \hbar}_{2}$$

Δp = uncertainty in momentum: Δx = uncertainty in position
ΔE = uncertainty in energy: Δt = uncertainty in time

to understand consider the first quantum state of the square well problem (above)

• by definition the square well confines the e to a region of space of

$$\boxed{\Delta x = L}$$

• for n =1 momentum $|p| = h/2L$

both $\longleftarrow -p$ *and* $+p \longrightarrow$ are present in equal amounts

so $\Delta p = 2|p| = \dfrac{h}{L}$

• • therefore $\Delta p\ \Delta x = \left(\dfrac{h}{L}\right) L = h \geq \hbar$

$\Rightarrow$**true for n=1**
∞ square well

Consider 2nd level of ∞ square well

$$\Delta x = L \text{ still}$$

$$\text{but now } \quad p = \left(2\frac{h}{2L}\right)$$

$$\leftarrow -p_2 \qquad +p_2 \rightarrow$$

$$\text{so } \Delta p = 2\left(\frac{h}{L}\right)$$

$$\Delta x \Delta p = (L)\frac{2h}{L} = 2h$$

same

Has increased

recall

for 1st level of ∞ square well

$$\Delta x \Delta p = (L)\frac{h}{L} = h$$

Energy-time uncertainty

$$\Delta E = E(p+\Delta p) - E(p) = (p+\Delta p)^2/2m - p^2/2m$$

$$= p^2/2m + 2\,p\,\Delta p/2m + \Delta p^2/2m - p^2/2m$$

$$= 2\,p\,\Delta p/2m \qquad + \{\cancel{\Delta p^2/2m}\}$$

this {} term very small so drop

$\underline{\text{so } \Delta E = 2\,p\,\Delta p/2m}$ will use below

we know $p = m\underbrace{v = m\,\Delta x/\Delta t}$ and $\Delta p = h/\Delta x$ (from above)

therefore $\Delta E = p\,\Delta p/m = m\,(\Delta x/\Delta t)\,(h/\Delta x)/m = h/\Delta t$

∴ therefore $\Delta E\ \Delta t = h \geq \hbar$

$\Rightarrow$**True for free e^-**

in general true for mater waves !!

"spin" of the electron

- **classical argument useful (<u>and wrong</u> !) - view of the spin/magnetic moment of e^-**

  - imagine e^- as spinning sphere of " –" charge

  - the circular electrical current from this spinning will create magnetic field (or a magnetic moment)

  - the magnetic moment will be proportional to the angular momentum

Although the above is not a proper picture, the e^- does possess <u>a spin angular momentum</u> and <u>magnetic moment</u>

e^- spin angular momentum $\quad \mathbf{s}\hbar \quad\quad \mathbf{s} = \frac{1}{2}$ **spin quantum number**

choose a z direction in space projection of $\mathbf{s}\hbar$ **along z is quantized**

$$\hbar\, \mathbf{s}_z = \mathbf{m}\hbar \qquad\qquad \mathbf{m} = +\frac{1}{2}, \quad -\frac{1}{2}$$

$\uparrow$ **spin up** $\quad \downarrow$ **spin down**

What happens when there is more than 1 e^- in a quantum problem?

Pauli Exclusion Principle !!!

- **No 2 electrons* can occupy the same "state"**

*** Fermions = protons, neutrons, …**

or

- **No 2 electrons* can occupy the same space (have identical wave functions) at the same time**

or

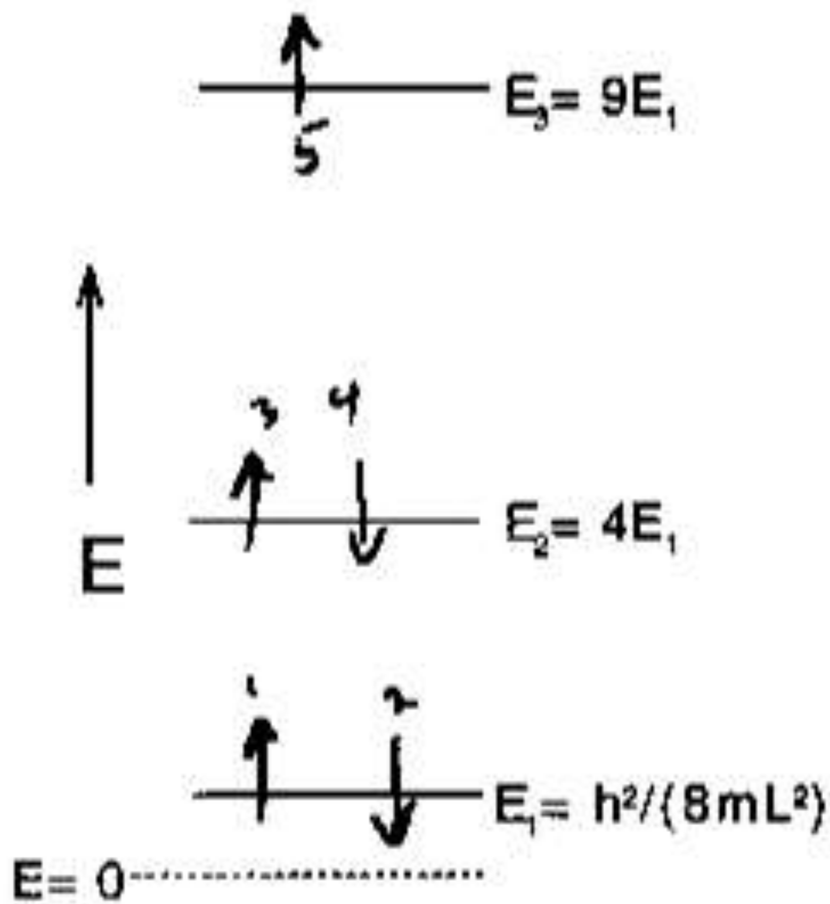
- **No 2 electrons* can have all the same quantum numbers. (this includes the spin quantum number)**

Consider: Pauli Exc. Princ. + spin in infinite square well problem

Example: Consider the lowest energy for 5 electrons in the infinite square well problem.

↑ = spin up

↓ = spin down



$1 \cdot 9E_1$

$2 \cdot 4E_1$

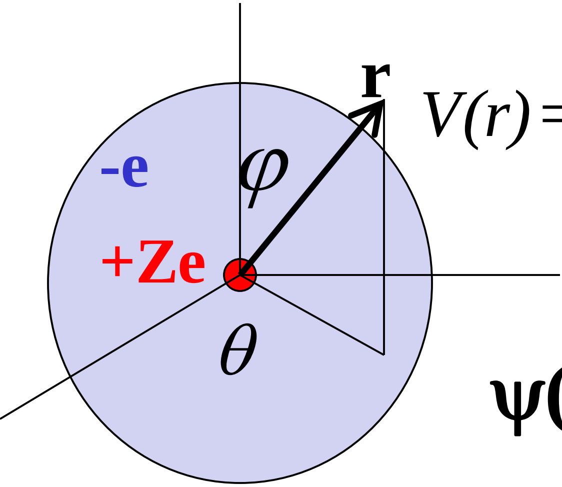
$2E_1$

$19E_1$

Thus the lowest energy is

$2E_1 + 2E_2 + 1E_3 = 2E_1 + 2(4E_1) + (9E_1) = 19E_1$

Quantum hydrogen atom



$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

Schrödinger equation

$$\frac{\mathbf{p}^2}{2\mathbf{m}}\psi + \mathbf{V(r)}\psi = \mathbf{E}\psi$$

$$\mathbf{p}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Actually use spherical coordinates

solution

$$\psi(r,\theta,\varphi) = R(r)_{n,l}\ Y_{n,l}(\theta,\varphi)$$

Spherical Harmonics

- **1 electron states**

  n = principal quantum number (1, 2, 3, …)

  l = angular momentum (0, 1, 2, … n-1)

  m_ℓ = z component of l (-l < m_l < l)

  m_s = z component spin (-½ , +½)
- **Pauli Exclusion Principle explains periodic table**
- **Shells fill in order, according to lowest energy.**

associated Laguerre polynomials $\quad R(r)_{n,l} = r^l\ L(r)_{n,l}\, e^{-r/na_o}$

Atomic Quantum Physics and Quantum Numbers

Schrödinger Eq.

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

boundary condition $\Psi(\infty)=0$

Solve

$$\boxed{E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{Z^2}{n^2} \qquad \text{n = 1, 2, 3 principal quantum number}}$$

E conserved

E quantized

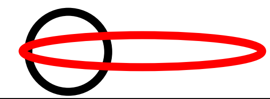
Central force- angular momentum =L conserved L quantized – remember

$$\boxed{L = \hbar\sqrt{l(l+1)} \quad l = 0,\ 1\ , \ldots, (\text{n-1}) \quad \text{orbital/ang.-mom. quantum number}}$$

Bohr !

[l=0 and L=0 are lowest – no angular momentum !!!!!- e- path through r=0 & nucleus (Bohr wrong)]

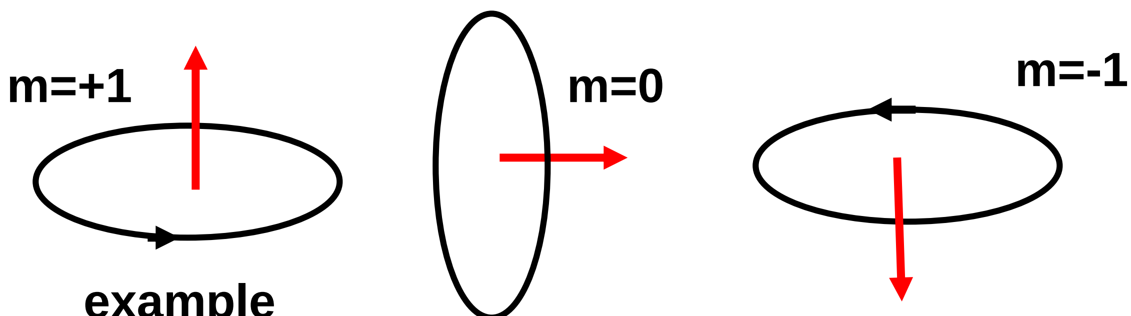
[classically – more eccentric orbit (directional) higher angular momentum orbit]



Orientation of orbit [conserved – constant for central force]⇒ z-component of ang. mom. (L_z)Conserved & quantized

$$\boxed{L_z = m_l\hbar}$$

m_l= *l* , *l*-1, *l*-2 , … , - *l*



- **QM- electron spin “Up” or “Down”**

$$\boxed{\text{m}_\text{s} = \text{Spin Quantum Number } (-½\ ,\ +½)}$$

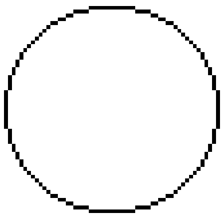
$$L = \hbar\sqrt{l(l+1)}$$

$$\ell = 0,\ \mathbf{\mathit{1}}\ ,\ \mathbf{\mathit{2}},\ \mathbf{\mathit{3}},\ \ldots,\ \mathbf{\mathit{(n\text{-}1)}}$$

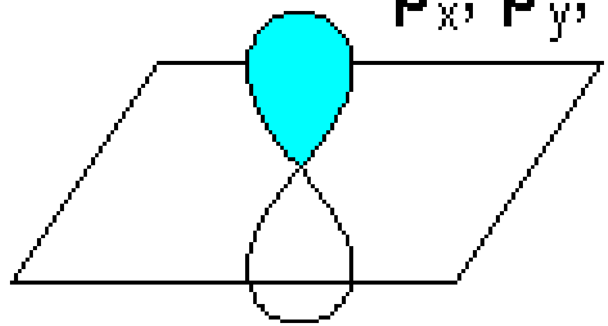
call s, p, d, f

s, p, d wave functions have different angular probability

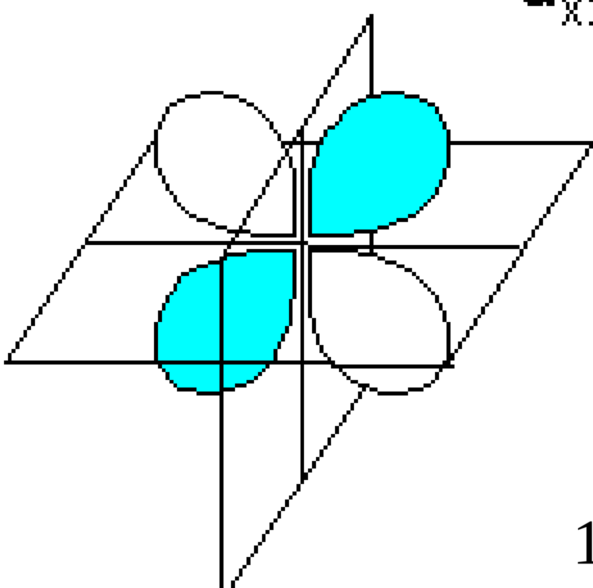
-charge distribution



s

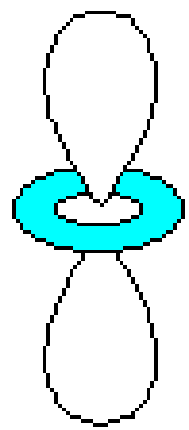


p_x, p_y, p_z



d_{xz}, d_{yz}, d_{xy}

d_{x2-y2}



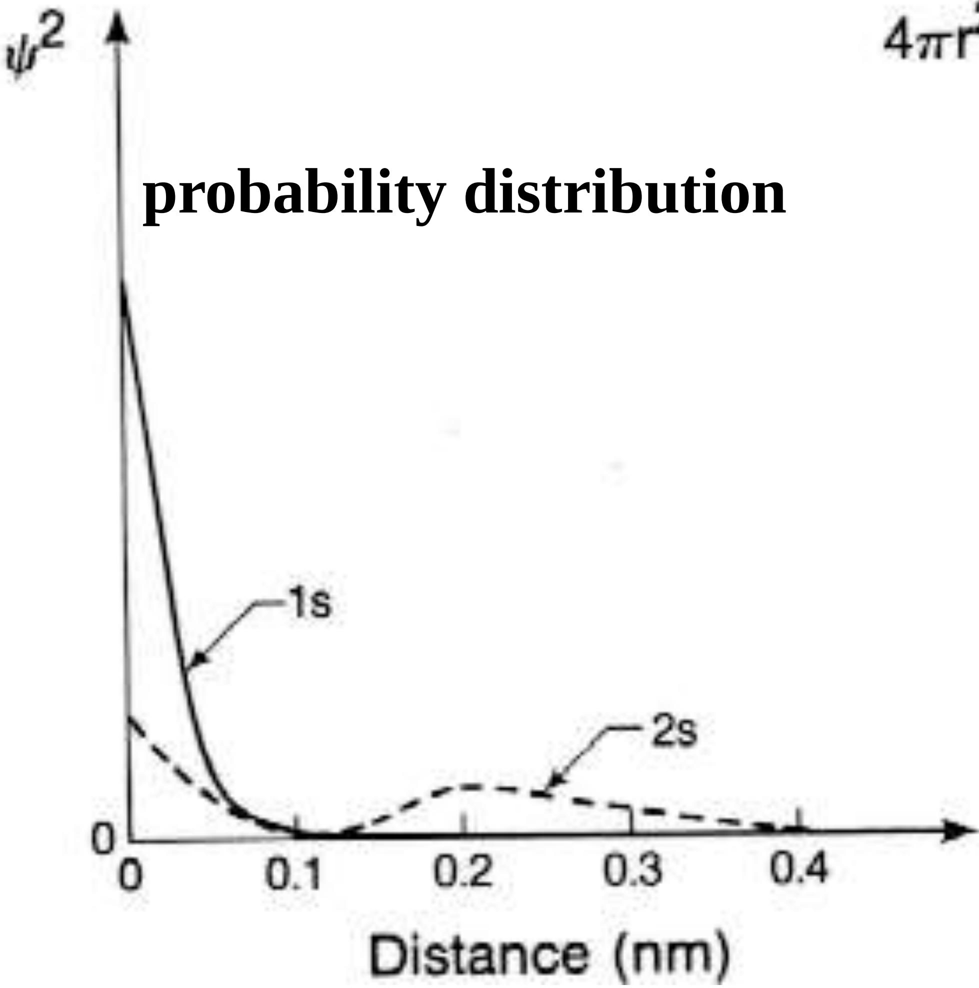
d_{z2}

http://winter.group.shef.ac.uk/orbitron/

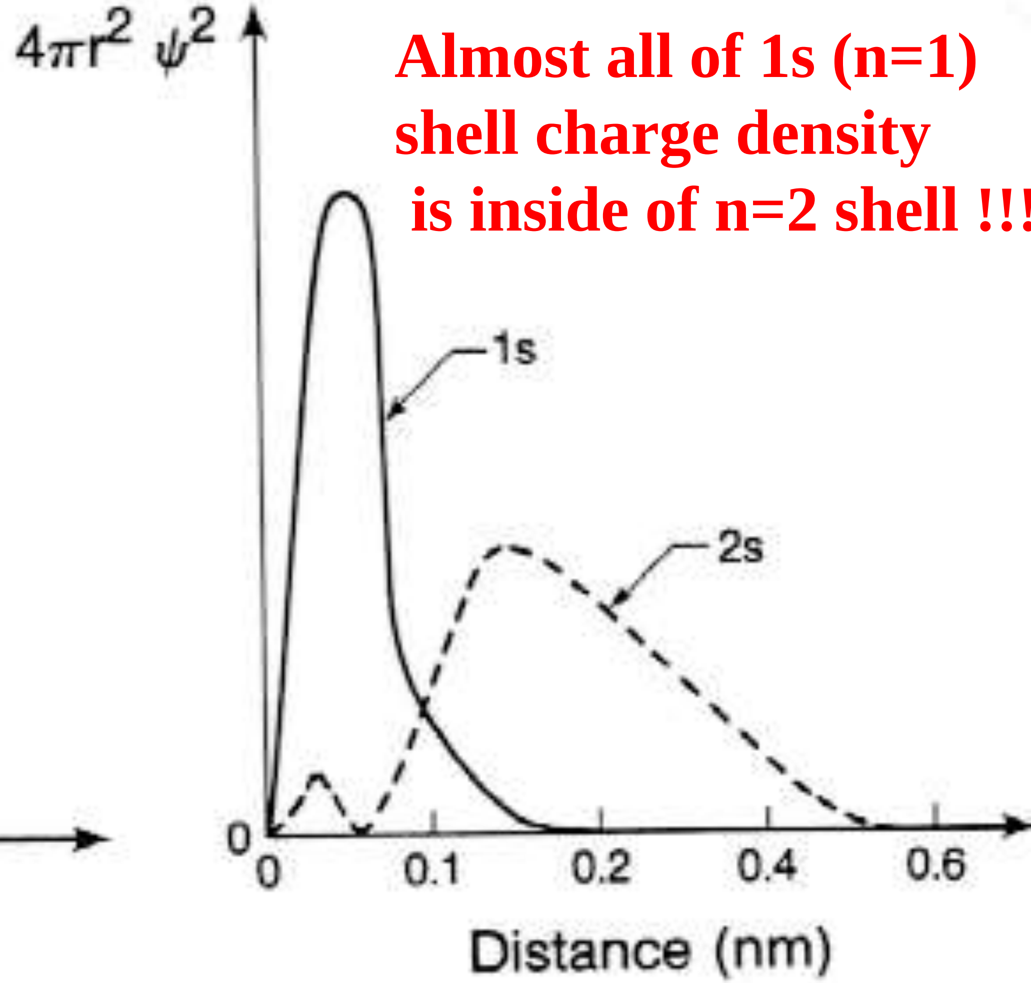
Atomic shell structure

$4\pi r^2 \psi^2$ ~ radial probability distribution in shell at r ~ charge density

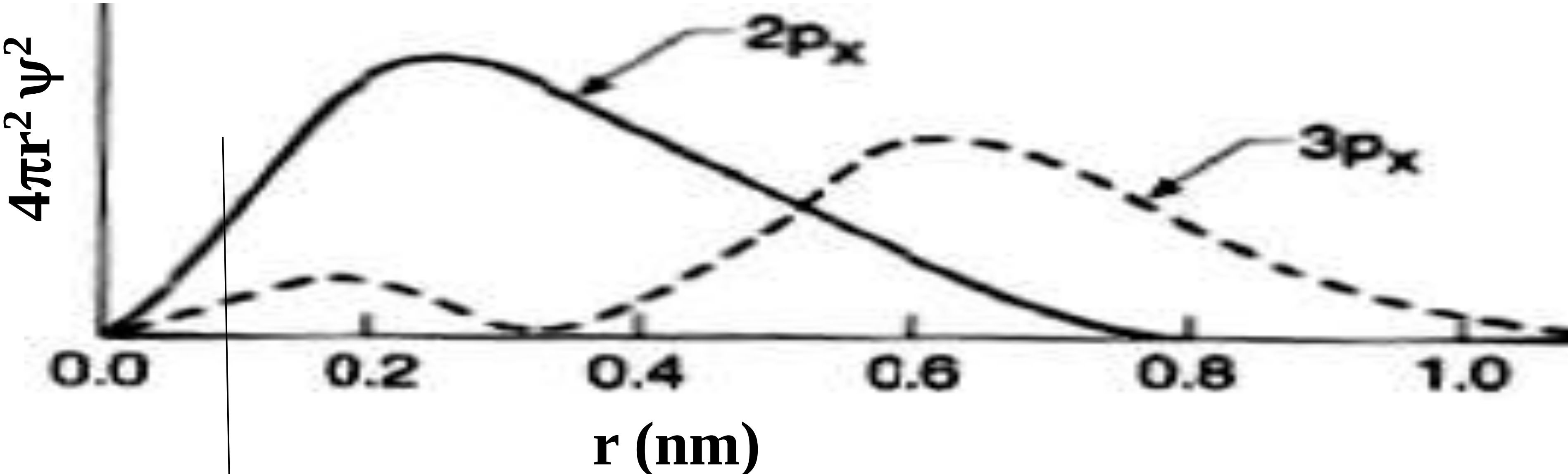
probability distribution

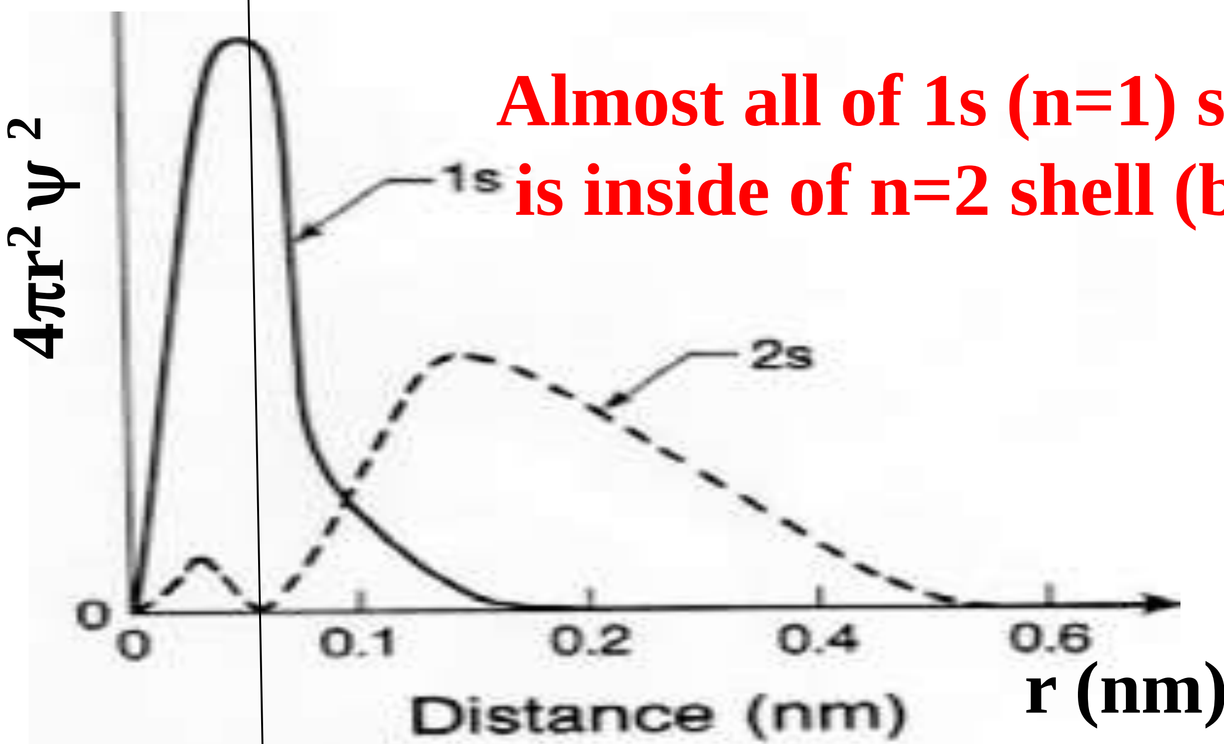


Almost all of 1s (n=1) shell charge density is inside of n=2 shell !!!



$4\pi r^2 \psi^2$ ~ radial probability distribution ~ charge density





Almost all of 1s (n=1) shell charge density is inside of n=2 shell (both s and p) !!!

Atomic Physics (very Briefly)

Bohr Theory $E_n = \frac{-13.6\ eV}{n^2} Z^2 \quad n = 1, 2, 3, \ldots$

Full Schrödinger Theory for QM of atom

- $E_n \approx E_n(\text{Bohr}) \qquad n = 1, 2, 3, \ldots$

  $n =$ principal quantum #

- Angular Momentum $\vec{L}$ quantized

  $L = \sqrt{\ell(\ell+1)}\,\hbar \qquad \ell = 0, 1, 2, \ldots \leq (n-1)$

examples

$n = 1 \quad \ell = 0$

$n = 2 \quad \ell = 0,\ \ell = 1$

$n = 3 \quad \ell = 0,\ \ell = 1,\ \ell = 2$

- Magnetic Quantum # m_ℓ

  L_z = projection of angular momentum along z direction

  $$L_z = m_\ell \hbar$$

  $$m_\ell = +\ell, (\ell-1), \ldots, 0, \ldots (-\ell+1), -\ell$$

  example

  $\ell = 0 \quad m_\ell = 0$

  $\ell = 1 \quad m_\ell = +1, 0, -1$

  $\ell = 2 \quad m_\ell = -2, -1, 0, 1, 2$

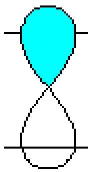
Now add spin quantum number

$$s_z = m_s \hbar \qquad m_s = \pm \frac{1}{2}$$

$n = 1$ $\quad$ $[\ell = 0$ (s), $m_\ell = 0$, $m_s = \pm\frac{1}{2}$ — can take $2e^-$ $\quad$ H He

---

$n = 2$ $\quad$ same $\rightarrow [\ell = 0$, $m_\ell = 0$, $m_s = \pm\frac{1}{2}$ — $2e^-$ $\quad$ Li Be



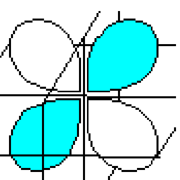
$[\ell = 1 \quad m_\ell = -1$, $m_s = \pm\frac{1}{2}$

$\quad\quad m_\ell = 0$, $m_s = \pm\frac{1}{2}$

$\quad\quad m_\ell = +1$, $m_s = \pm\frac{1}{2}]$ — $6e^-$ $\quad$ B C N O F Ne

p

$n = 3$ $\quad \rightarrow$ [same]



$\ell = 2 \quad m_\ell = -2 \quad m_s = \pm\frac{1}{2}$

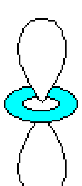
$\quad\quad -1$

$\quad\quad -0$

$\quad\quad 1$

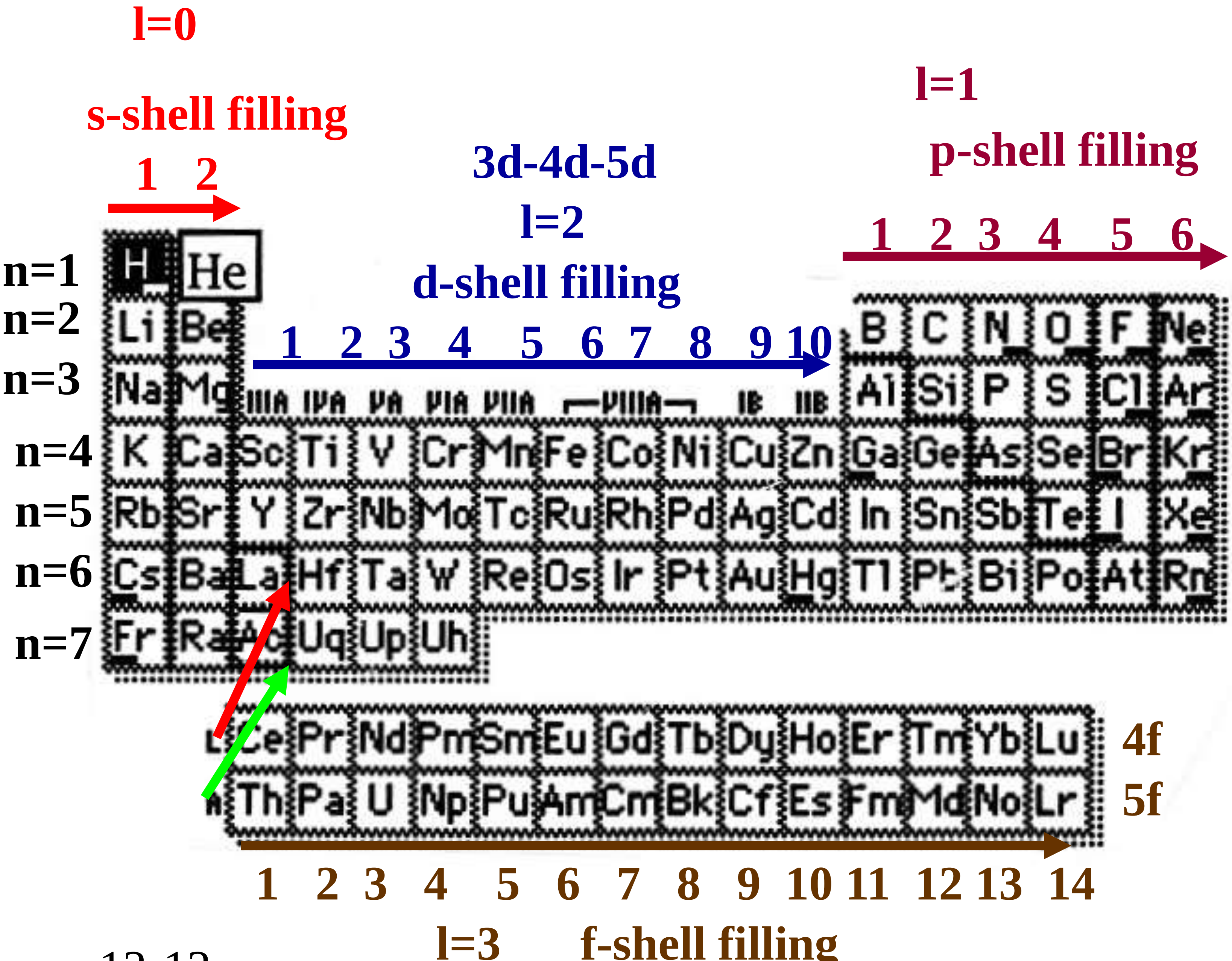
$\quad m_\ell = 2 \quad m_s = \pm\frac{1}{2}$ — d $\quad 10e^-$

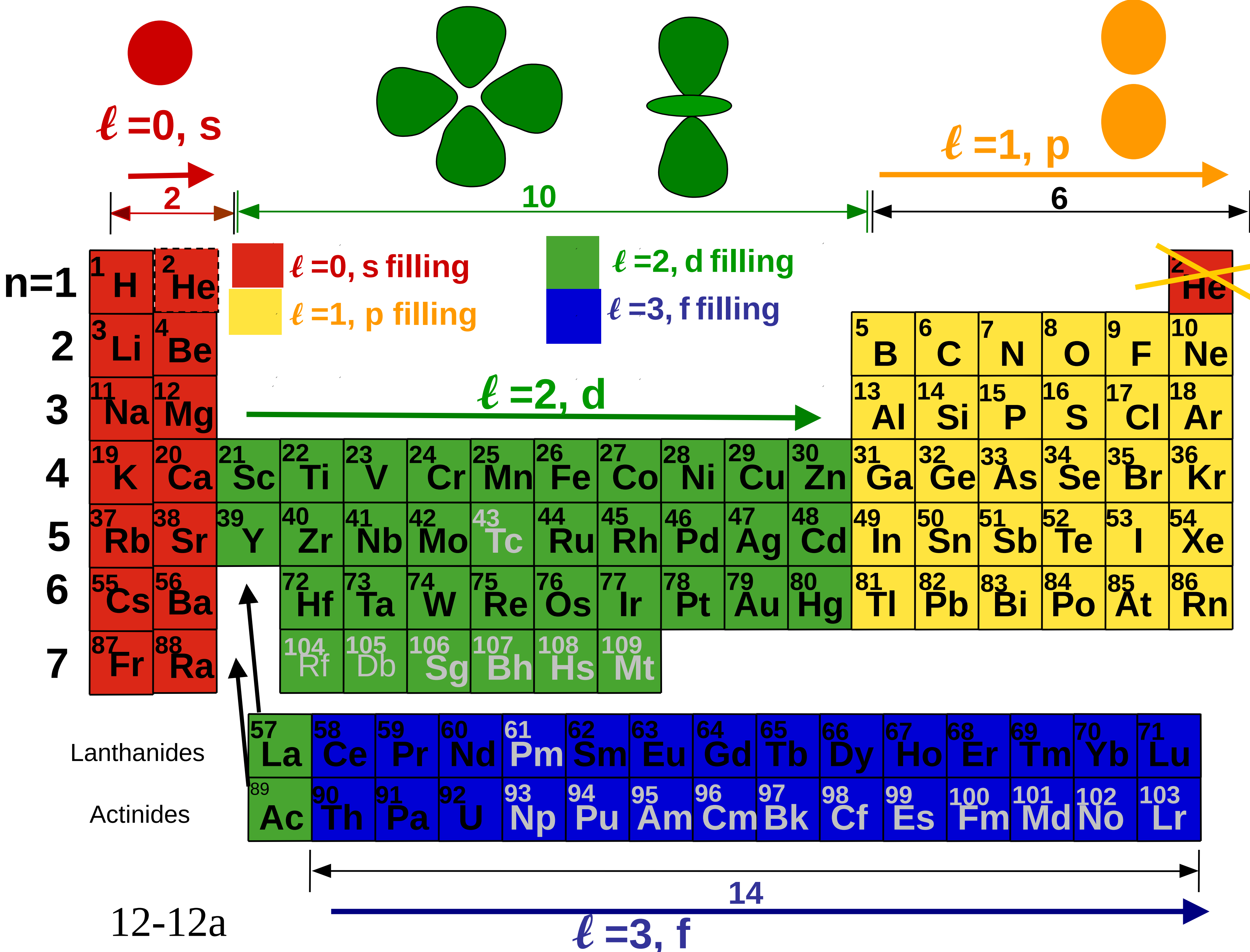
Sc Ti V Cr Mn Fe Co Ni Cu Zn



12-11

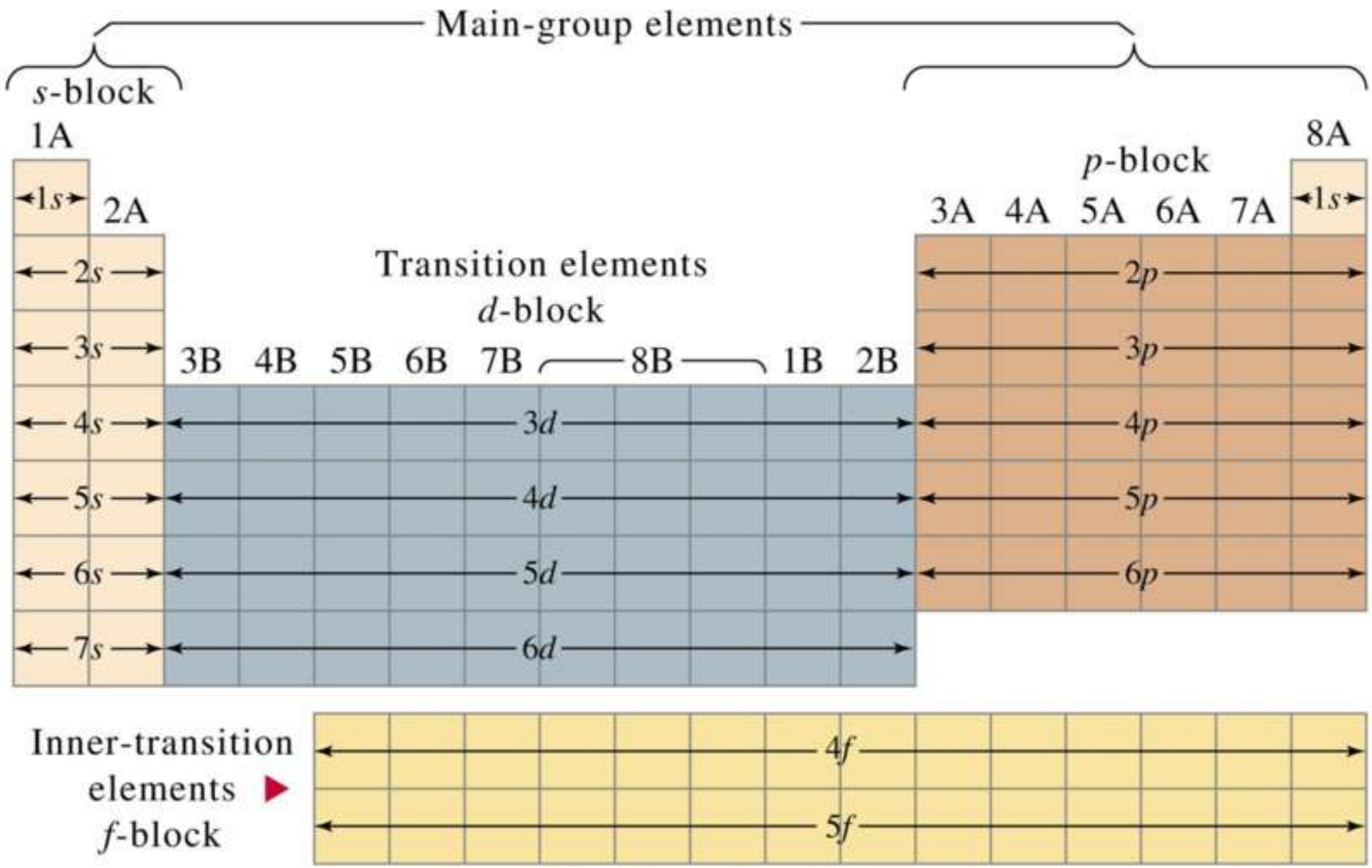
http://phet.colorado.edu/en/simulation/build-an-atom





ℓ =0, s
2
10
6
ℓ =1, p
ℓ =0, s filling
ℓ =1, p filling
ℓ =2, d filling
ℓ =3, f filling
n=1
2
3
4
5
6
7
1 H 2 He
3 Li 4 Be
11 Na 12 Mg
19 K 20 Ca
37 Rb 38 Sr
55 Cs 56 Ba
87 Fr 88 Ra
ℓ =2, d
21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn
39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd
72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg
104 Rf 105 Db 106 Sg 107 Bh 108 Hs 109 Mt
2 He
5 B 6 C 7 N 8 O 9 F 10 Ne
13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
Lanthanides
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
Actinides
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
14
ℓ =3, f

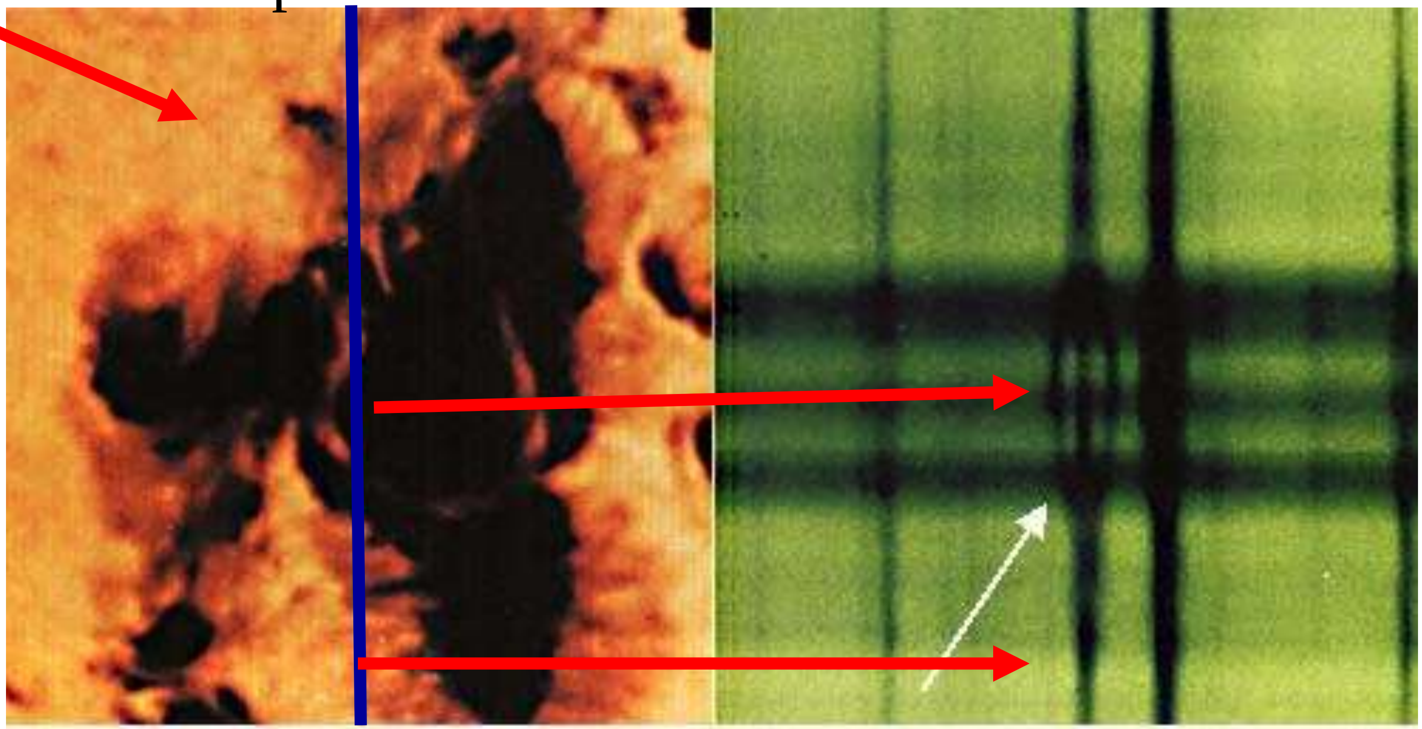
12-12a



Main-group elements
s-block
1A
2A
1s
2s
3s
4s
5s
6s
7s
p-block
8A
3A 4A 5A 6A 7A
2p
3p
4p
5p
6p
Transition elements
d-block
3B 4B 5B 6B 7B 8B 1B 2B
3d
4d
5d
6d
Inner-transition
elements
f-block
4f
5f

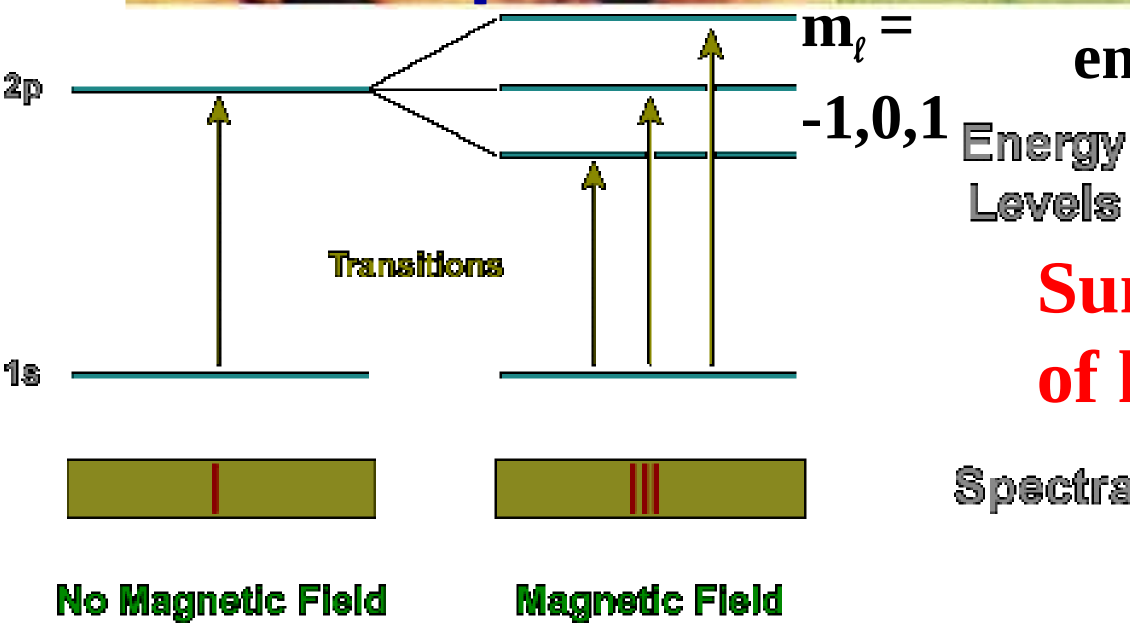
12-12b

Picture of Sunspot on sun



Spectrum along line through sunspot

14.9



energy →

Sun spots are regions of high magnetic fields !!!