



# Quantum Physics PY1T20/PYU11P20

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## Quantum Physics Lecture 14

### The Hydrogen atom

- Solution of Schroedinger equation
- 3 spatial quantum numbers
- Probability and 'Orbitals'
- Selection rules for transitions
  
- Zeeman effects (non-exam), electron spin
- 4 quantum numbers
  
- Atomic structure beyond hydrogen : the periodic table

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# Hydrogen Atom Re-visited

First real test of Schroedinger Equation:

Recall Bohr model:  $E_n \propto -1/n^2$ , via one quantum number  $n$   
(also, quantised angular momentum  $L$  via same  $n$ )

$$L_{\text{Bohr}} = n\hbar$$

**Successes:** Hydrogen line emission spectra  
also... size & stability of atoms, Moseley's Law for  $Z$ , etc.

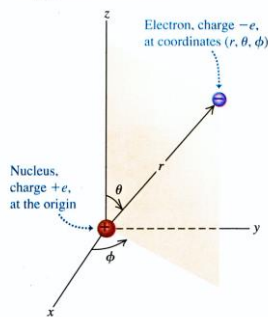
**Problems:** Full 3D & spherical symmetry?  
Magnetic effects in spectra  
 $Z > 1$  atoms' spectra

Comparison with Bohr model:  
same expression for  $E_n$  via "principal" quantum number  $n$

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## Schroedinger Equation for H atom

**41.5** The Schrödinger equation for the hydrogen atom can be solved most readily using spherical coordinates.



Express wavefunction as product (cf 2-D box)

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

Leads to 3 separate equations

$$-\frac{\hbar^2}{2mr^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left( \frac{\hbar^2 l(l+1)}{2mr^2} + U(r) \right) = ER(r)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left( l(l+1) - \frac{m_l^2}{\sin^2(\theta)} \right) \Theta(\theta) = 0$$

$$\frac{d^2\Phi(\phi)}{d\phi^2} + m_l^2\Phi(\phi) = 0$$

$R$  solutions are  $e^{-ar}$  ( $\times r$  polynomial) type,  $\Theta$  are functions of  $\cos$  &  $\sin \theta$   
 $\Phi$  solutions are  $\exp(im_l\phi)$  type, where  $m_l$  is an integer

Solutions specified by three quantum numbers:  $n, l, m_l$

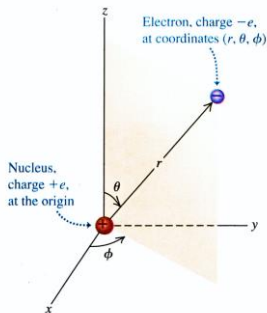
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## Schroedinger Equation for H atom: relation to angular momentum

**41.5** The Schrödinger equation for the hydrogen atom can be solved most readily using spherical coordinates.

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left( l(l+1) - \frac{m_l^2}{\sin^2(\theta)} \right) \Theta(\theta) = 0 \quad L^2 f = \hbar^2 l(l+1) f$$

$$\frac{d^2 \Phi(\phi)}{d\phi^2} + m_l^2 \Phi(\phi) = 0 \quad L_z f = \hbar m_l f$$



Same as equations defining  $f(\Theta, \phi) = \Theta(\theta)\Phi(\phi)$  as an eigenfunction of the angular momentum operators

$\Rightarrow$  The quantum numbers  $l$  and  $m_l$  are the 'magnitude' and 'projection' of the angular momentum of the electron

*Info: this is not a coincidence! The energy (Hamiltonian) does not depend on angles, so the angular momentum is conserved. In quantum mechanics, this means the eigenfunctions of the Hamiltonian (=stationary states) are also eigenfunctions of angular momentum.*

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## Schroedinger Equation for H atom (cont.)

As asserted in lecture 13, we must have

$l=0, 1, 2, 3$  for a sensible (normalizable) solution.

Corresponding to magnitudes of a.m. in each case

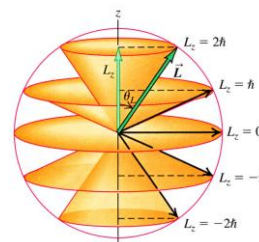
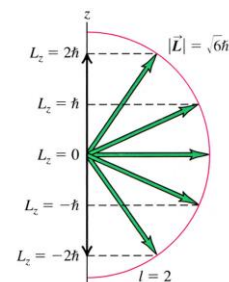
$$|L| = \hbar \sqrt{l(l+1)}$$

Also  $\Phi$  must be single valued so  $m_l$  integer ( $\Phi(\phi) = \Phi(\phi + 2\pi)$ )

and normalizable solution only if  $-l \leq m_l \leq l$

Note  $l=0$  (and  $m_l=0$ ) is allowed, unlike the Bohr model.

Also 'direction of a.m.' is not well-defined (see lecture 13), unlike Bohr model. Magnitude (squared) is : angular momentum is conserved



'Semi-classical' vector pictures for  $l=2$

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## Schroedinger Equation for H atom (cont.)

Solutions specified by three quantum numbers:  $n, l, m_l$  (c.f. 3-D box, Lect. 9)

Energy Levels are  $E_n$  and the same as the Bohr model!

with  $n = 1, 2, 3, 4, \dots$

Normalizable solutions need  $l = 0, 1, 2, 3 \dots n-1$  and  $|m_l| \leq l$

Notation:  $s, p, d, f \dots$  for  $l = 0, 1, 2, 3, \dots$

So, possible states of electron:

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n^2} \right)$$

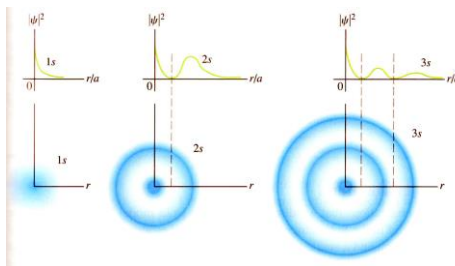
Note:  $E_n$  does not depend on  $l, m_l$   
i.e.  $l, m_l$  states are degenerate –  
but holds only for H atom

**Table 41.1 Quantum States of the Hydrogen Atom**

$n$	$l$	$m_l$	Spectroscopic Notation	Shell
1	0	0	1s	K
2	0	0	2s	L
2	1	-1, 0, 1	2p	
3	0	0	3s	M
3	1	-1, 0, 1	3p	
3	2	-2, -1, 0, 1, 2	3d	
4	0	0	4s	N
and so on				

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## Electron states in hydrogen atom - orbitals



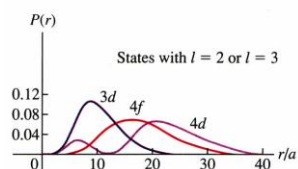
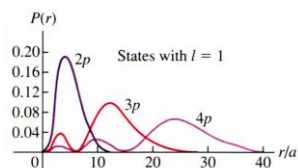
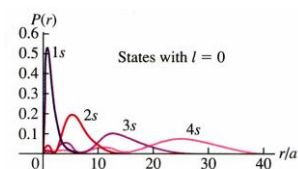
s-states - spherically symmetric

Radial probability distributions ( $a = \text{Bohr radius}$ )

Note for  $l = n-1$  (1s, 2p, 3d...) there is one maximum, at  $r = n^2 a$

Generally the number of zeros of  $R(r)$  away from  $r=0$  is  $n-l-1$ .  
s functions are non-zero at  $r=0$ . all others are zero at  $r=0$ .

$$P(r)dr = |\psi|^2 4\pi r^2 dr$$



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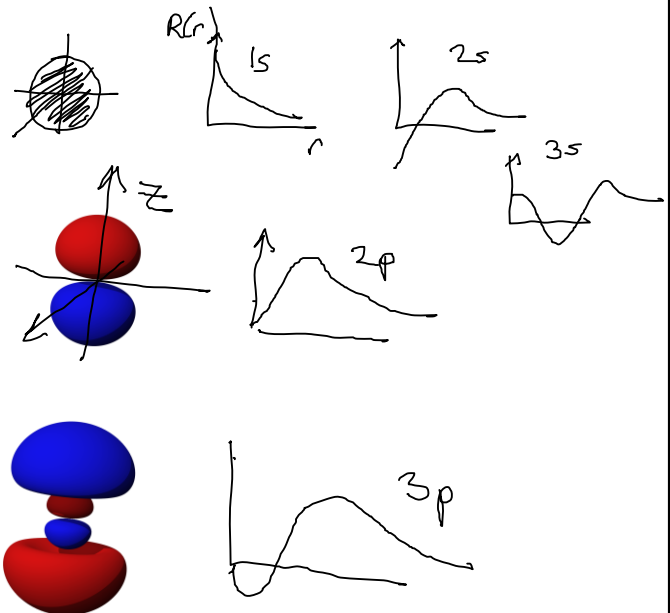
## Angular functions - orbitals

s orbitals are easy – spherically symmetric

three p orbitals,  $m_l=1, 0, -1$ .

wavefunction for 2p with  $m_l=0$  are real  
(contours with red/blue +/-)

3p with  $m_l=0$  (one more radial node than 2p) :

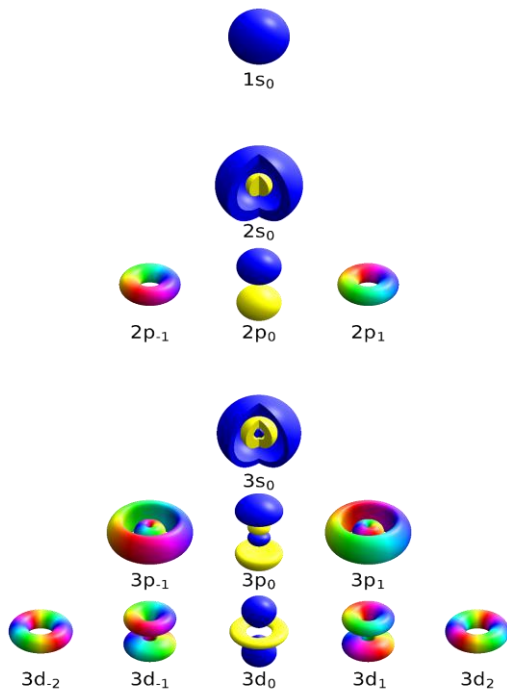


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## Angular functions - orbitals

Other orbitals are complex, e.g.  $m_l=+1, -1$ .

Plotted as contours surfaces of magnitude with  
colouring by argument/phase (at surface) :



[http://en.wikipedia.org/wiki/Atomic\\_orbital](http://en.wikipedia.org/wiki/Atomic_orbital)

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## Angular functions - orbitals

Consider 2p,  $m_l = -1$  and  $m_l = +1$

- Wavefunction is complex but we can make real combinations,
- $(m_l = +1) + (m_l = -1)$ , 'p<sub>x</sub> orbital', and
- $(m_l = +1) - (m_l = -1)$ , 'p<sub>y</sub> orbital.'

Can do for other orbitals too:

e.g. there are 5 3d orbitals. One is already real ( $m_l = 0$ ), and we can make 4 other real combinations.

These 'real' orbitals are important in chemistry and solid-state physics, because they tell you about the geometry of bonds – we have orbitals pointing in particular directions, which gives information about how/the directions bonds can form in.

	s ( $\ell = 0$ )	p ( $\ell = 1$ )			d ( $\ell = 2$ )				
	$m = 0$	$m = 0$	$m = \pm 1$		$m = 0$	$m = \pm 1$		$m = \pm 2$	
	s	p <sub>z</sub>	p <sub>x</sub>	p <sub>y</sub>	d <sub>z<sup>2</sup></sub>	d <sub>xz</sub>	d <sub>yz</sub>	d <sub>xy</sub>	d <sub>x<sup>2</sup>-y<sup>2</sup></sub>
n = 1									
n = 2									
n = 3									
n = 4									
n = 5									
n = 6					...	...	...	...	...
n = 7		...	...	...	...	...	...	...	...

[http://en.wikipedia.org/wiki/Atomic\\_orbital](http://en.wikipedia.org/wiki/Atomic_orbital)

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## Transition of electrons between orbitals

**Selection rules** for transitions:  $\Delta l = \pm 1$

And  $\Delta m_l = 0$  or  $\pm 1$


All others are 'forbidden'

Conservation overall of angular momentum,  
photon has angular momentum of  $\hbar$

$l$  determines the magnitude of  $L$ ,  
 $m_l$  determines the direction

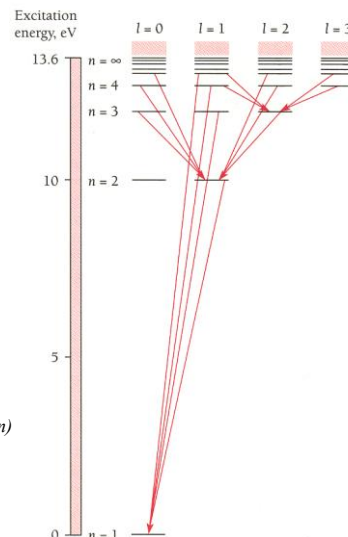
A non-zero magnetic field direction defines  $z$   
But B field alters the energy...

N.B. Magnetic dipole moment (current in loop  $\times$  area of loop)

  $\mu = \frac{ve}{2\pi r} \pi r^2$  with  $mvr = \hbar$        $\mu_B = \frac{e\hbar}{2m}$  (Bohr Magnetron)

So moment =  $m_l \mu_B$

Applied B field shifts energy (dipole-field interaction)  
so  $m_l$  states are split apart by  $\mu_B B$



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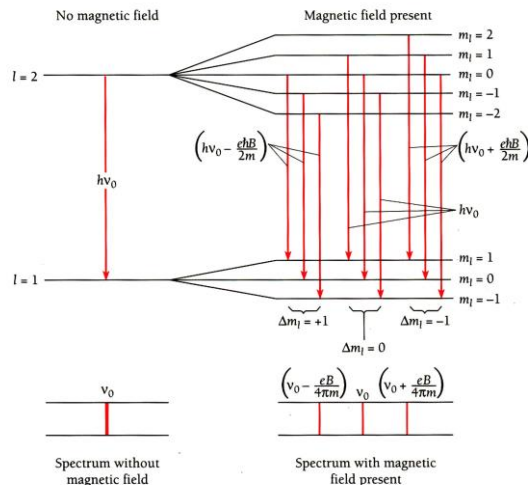
## Zeeman Effect

In non-zero magnetic field  $B$  each  $l$ -level splits into  $2l+1$   $m_l$  sub-levels of slightly different energy, depending on  $B$

Spectra show three lines instead of one; only three because of further selection rule:

$$\Delta m_l = \pm 1, 0$$

But.... some transitions showed more than three - anomalous

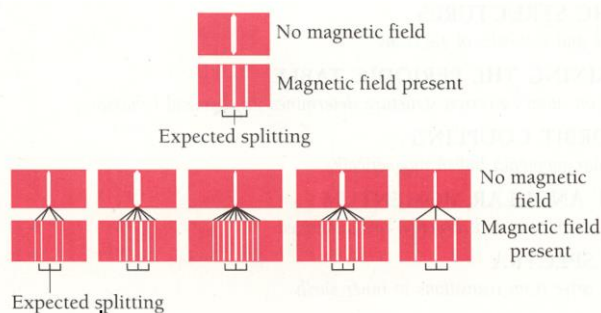


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## Anomalous Zeeman Effect

Problem: more than 3 lines and smaller separation(s)

Solution:  
"electron spin"  
*See lecture 13 !*



Electron has spin angular momentum  $s_z = \pm \frac{\hbar}{2}$  but  $\mu_z = -(2.000232) \frac{e}{2m} s_z$

Spin angular momentum  $S$  (*cf*  $L$ ) Spin magnetic quantum number  $m_s$  (*cf*  $m_l$ )

For info: Total combined angular momentum  $\vec{J} = \vec{L} + \vec{S}$

$J$  is an operator in quantum mechanics, which works like the other angular momentum. e.g. eigenvalues of  $J^2$  are  $\hbar^2 j(j+1)$  with  $j$  integer or half-integer. For spin-1/2,  $j = l \pm 1/2$   
Combining  $L$  and  $S$  leads to correct number and splitting of emission lines (*first seen by Irishman Thomas Preston*)

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## More than 1 electron atoms...

Simple picture:

can add electrons to hydrogen-like quantum states

*assumes the nucleus increasing charge is shielded by inner electrons  
and ignores electron – electron interaction energies....  
Try it anyway....*

But: Pauli exclusion principle – no two electrons can occupy the same quantum state  
(fermions, see Lecture 13)

Two spins states possible – ‘up’ and ‘down’  $\uparrow$  or  $\downarrow$  or  $z$  components  $\pm \frac{\hbar}{2}$

So maximum of two electrons in each state

one  $\uparrow$  and the other  $\downarrow$

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## Many electron atoms

For  $Z > 1$ , fill quantum states with max. 2 electrons each

First quantum number  $n$  (c.f. Bohr energy level)

Second quantum number  $l$  (angular momentum state) where  $0 \leq l \leq (n-1)$

Third quantum number  $m_l$  where  $|m_l| \leq l$

**Table 41.2 Quantum States of Electrons in the First Four Shells**

$n$	$l$	$m_l$	Spectroscopic Notation	Number of States	Shell
1	0	0	1s	2	K
2	0	0	2s	2	
2	1	-1, 0, 1	2p	6	L
3	0	0	3s	2	
3	1	-1, 0, 1	3p	6	M
3	2	-2, -1, 0, 1, 2	3d	10	
4	0	0	4s	2	N
4	1	-1, 0, 1	4p	6	
4	2	-2, -1, 0, 1, 2	4d	10	
4	3	-3, -2, -1, 0, 1, 2, 3	4f	14	

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## Z>1 The periodic table of elements

$n=1$  -  $l=0$  s state – 2 electrons  
 $n=2$  -  $l=1$  p state – 6 electrons  
 .....  $l=2$  d state – 10 electrons  
 .....  $l=3$  f state – 14 electrons

Gives the basic structure of the  
**Periodic Table** of the elements

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1																		2
2	3	4												5	6	7	8	9	10
3	11	12												13	14	15	16	17	18
4	19	20												21	22	23	24	25	26
5	37	38												39	40	41	42	43	44
6	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73
7	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105

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## Many electron atoms (cont.)

Examples: Helium atom

Contains 2 electrons, both can be in 1s state (*lowest energy*)  
provided one is spin up the other spin down

Notation for the ground state  $1s^2$

Lithium ( $Z=3$ )

1s shell filled (like He)

Extra electron goes into 2s shell

Notation  $1s^2 2s^1$

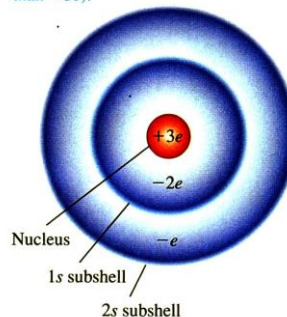
2s orbital further out...

Nuclear charge screened by 1s shell, effective charge more like H but further out

So less well bound

2s electron can be lost in bonding (ionicity)

On average, the 2s electron is considerably farther from the nucleus than the 1s electrons. Therefore, it experiences a net nuclear charge of approximately  $+3e - 2e = +e$  (rather than  $+3e$ ).



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# Periodic Table of Elements

Group	1	2																	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18								
Period																																										
1	1 H																																			2 He						
2	3 Li	4 Be																																			5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg																																			13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca																	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								
5	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								
6	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										
7	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	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	(117) Uus	118 Uuo										
1-7s		4-5f										3-6d										2-7p																				

For Hydrogen,  $s, p, d, f$ , states have same energy for given  $n$  (c.f. Bohr)

This **Degeneracy** of states is broken for  $Z > 1$  (by  $e-e$  interaction potentials)

So  $s$  generally fills before  $p$ , before  $d$  etc., the gap increasing as  $Z$  becomes larger.

Actual rule is : fill smallest  $(n+l)$  first, if tied, choose smallest  $n$ . (Some minor exceptions).