



Quantum Theory of Angular Momentum and Atomic Structure

Motivation...the questions

● Whence the periodic table?

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078											gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62											indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *										thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po (209)	astatine 85 At (210)	radon 86 Rn (222)
francium 87 Fr (223)	radium 88 Ra (226)	89-102 **															
			scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39					
			yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc (98)	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41					
			lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59					
			lawrencium 103 Lr (262)	rutherfordium 104 Rf (261)	dubnium 105 Db (262)	seaborgium 106 Sg (266)	bohrium 107 Bh (264)	hassium 108 Hs (269)	meitnerium 109 Mt (268)	darmstadtium 110 Ds (271)	ununium 111 Uuu (272)	ununbium 112 Uub (277)					
													ununseptium 114 Uuq (289)				

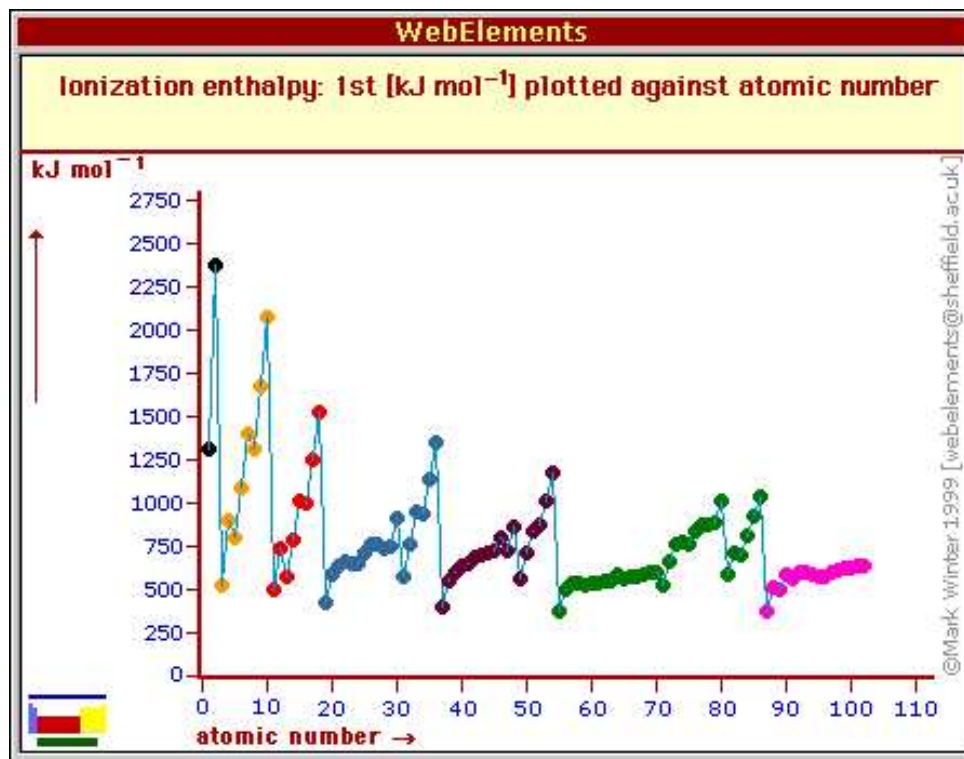
*lanthanoids

**actinoids

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm (145)	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac (227)	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np (237)	plutonium 94 Pu (244)	americium 95 Am (243)	curium 96 Cm (247)	berkelium 97 Bk (247)	californium 98 Cf (251)	einsteinium 99 Es (252)	fermium 100 Fm (257)	mendelevium 101 Md (258)	nobelium 102 No (259)

Motivation...the questions

- “Material” Music – Patterns in Periodic Table



- Rotational spectra of molecules

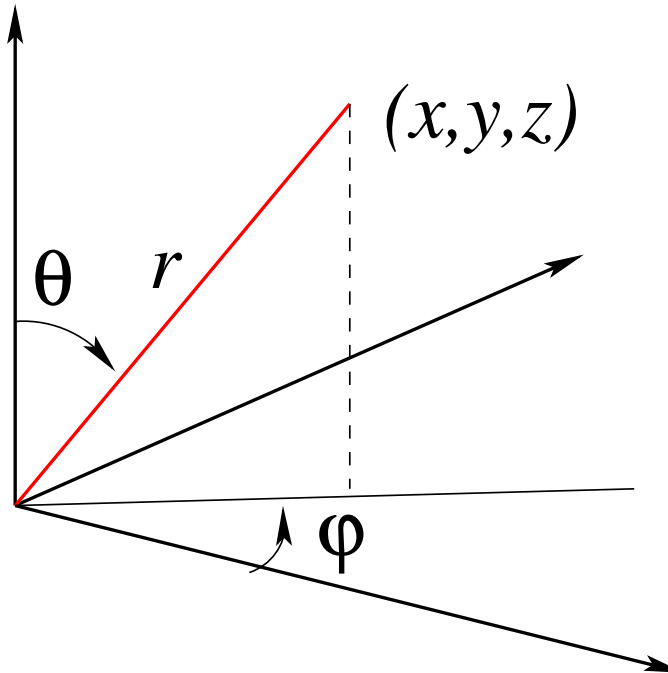


Model of Hydrogen Atom

- Fix the nucleus at origin
- Hamiltonian $H = \frac{P_x^2 + P_y^2 + P_z^2}{2m} + V(r)$, $r = \sqrt{x^2 + y^2 + z^2}$,
 $V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$
- Can we estimate ground state energy? Yes, we can!
- Boundstate...electron found within ℓ of nucleus
- Kinetic energy (uncertainty principle) $\sim \frac{\hbar^2}{2m\ell^2}$
- Potential energy $\sim -\frac{1}{4\pi\epsilon_0} \frac{e^2}{\ell}$
- $E_g(\ell) = \frac{\hbar^2}{2m\ell^2} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{\ell}$
- Ground state energy estimate $-\frac{1}{2} \frac{me^4}{(4\pi\epsilon_0)^2 \hbar^2} = -13.5\text{eV!}$

Spherical Polar Coordinates

- Alternate way of describing points in space



$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

- Suited for spherically symmetric problems



A different look at the Hamiltonian

- Classical kinetic energy $H = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r)$
- L^2 - magnitude square of the angular momentum
- In Quantum Mechanics L^2 is an operator
- In fact, L , the angular momentum vector is an operator
- What is the position representation of L ?
- In Cartesian coordinates, $L_x = YP_z - ZP_y$ etc...
- See more details later



Hamiltonian in Polar Representation

- If $|\psi\rangle$, is an energy eigenket, the wavefunction $\langle r, \theta, \phi | \psi \rangle = \psi(r, \theta, \phi)$ satisfies

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r} \frac{\partial^2 (r\psi)}{\partial r^2} \right) + \frac{1}{2mr^2} \left[\underbrace{-\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)}_{L^2!} \psi \right] + V(r)\psi =$$

- Can be thought of as

$$\left(\frac{P_r^2}{2m} + \frac{1}{2mr^2} L^2 + V(r) \right) \psi = E\psi$$



Hamiltonian in Polar Representation

- Try the ansatz, $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$
- If Y is eigenfunction of L^2 , then $L^2Y = \ell(\ell + 1)\hbar^2Y$ (eigenvalues written anticipating results)
- The radial part then satisfies the equation

$$\left(\frac{P_r^2}{2m} + \frac{\hbar^2\ell(\ell + 1)}{2mr^2} + V(r)\right)R = ER$$

- What are the allowed values of ℓ , and E ?



Angular Momentum

- What are the eigenstates of L^2 ?
- L^2 commutes with the Hamiltonian, $[L^2, H] = 0$...Rotational kinetic energy is conserved since no one is applying any torque!
- What about L ? Is it conserved?...should be!
- Lets see...with a bit of painful algebra

$$L_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right)$$

$$L_y = -i\hbar \left(\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)$$

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$



Angular Momentum

- It can now be shown that $[L_x, H] = 0$ and $[L_x, L^2] = 0$, similarly for y and z
- So angular momentum will be conserved!
- But there is more...very importantly
$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y$$
- This means that all components of angular momenta cannot be determined simultaneously without uncertainty!
- Since $[L_z, L^2] = 0$, we can choose eigenstates of L^2 and L_z simultaneously...and this is what we will do



Angular Momentum

- It turns out that the eigenstates are given by $Y_\ell^m(\theta, \phi)$ such that

$$L^2 Y_\ell^m(\theta, \phi) = \hbar^2 \ell(\ell + 1) Y_\ell^m(\theta, \phi), \quad L_z Y_\ell^m(\theta, \phi) = m\hbar Y_\ell^m(\theta, \phi),$$

- ℓ can take only non-negative integer values (0,1,2..etc)
- For a given value of ℓ , m can take values between $-\ell$ and ℓ ...and thus $2\ell + 1$ states
- Angular energy state given by ℓ is therefore $2\ell + 1$ fold degenerate



Angular Momentum Eigenstates

- The function $Y_\ell^m(\theta, \phi)$ are called “spherical harmonics”
- They satisfy $\int Y_\ell^m(\theta, \phi) Y_{\ell'}^{m'}(\theta, \phi) d\Omega = \delta_{\ell\ell'} \delta_{mm'}$ (no surprise there!)
- Related to Legendre polynomials (look up somewhere, Pauling-Wilson, for example)



Angular Momentum Eigenstates

- Some examples (how do you interpret this?)

- $\ell = 0$

$$Y_0^0 = \frac{1}{\sqrt{\pi}}$$

- $\ell = 1$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_1^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

- $\ell = 2$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \quad Y_2^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm i2\phi}$$



“Understand” Angular Momentum

- If you put a particle in the state given by ℓ, m , you will have a definite value of L^2 and L_z ...measurement of these quantities in this state will produce no uncertainty
- What about L_x and L_y ?
- It can be shown that $\langle L_x \rangle = \langle \ell, m | L_x | \ell, m \rangle = 0$! (same of L_y)
- Thus $\Delta L_x^2 = \langle L_x^2 \rangle$ and $\Delta L_y^2 = \langle L_y^2 \rangle$
- Clearly $\Delta L_x^2 + \Delta L_y^2 = \langle L^2 \rangle - \langle L_z^2 \rangle = \hbar^2 (\ell(\ell + 1) - m^2)$



Angular Momentum - Main Ideas

- If you let a quantum particle live on a unit sphere,
 - “rotational energy” (L^2) states are given by $\ell(\ell + 1)\hbar^2$ (ℓ is a non-negative integer)
 - and put the particle in an ℓ state, you can specify but one component of angular momentum precisely...the other two cannot be specified; also, the component can be specified only as $m\hbar$ where m is an integer from $-\ell$ to ℓ
- Think of the same situation in a classical context...and feel how very different quantum mechanics is! Also, make sure that you understand how you get back all classical results from quantum mechanics (hint: go to large values of ℓ)



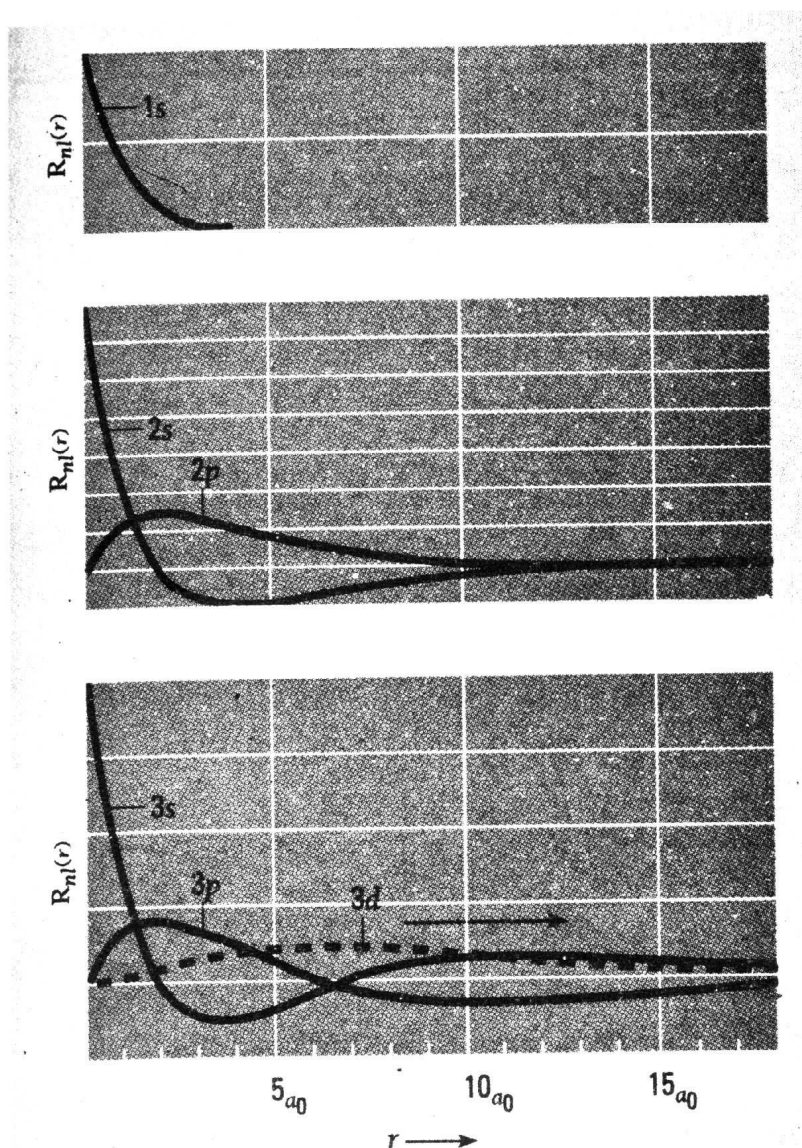
Back to Hydrogen Atom

- **Radial Equation** $\left(\frac{P_r^2}{2m} + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} + V(r) \right) R = ER$
- **Allowed values of E are** $E_n = -\frac{E_o}{n^2}$, $E_o = -13.5\text{eV}$, $n = 1, 2, \dots$
- **For each value of n , ℓ takes values between 0 and $n - 1$...tells us how energy is shared between radial and rotational degrees (contrast classical picture)!**
- **For a given n and ℓ , the radial wavefunction is**

$$R_n^\ell(r) = \sqrt{\left(\frac{2}{na_o}\right)^3 \frac{(n - \ell - 1)!}{2n[(n + \ell)!]^3}} e^{-\frac{r}{na_o}} \left(\frac{r}{na_o}\right)^\ell \mathcal{L}_{n+1}^{2\ell+1} \left(\frac{r}{na_o}\right)$$

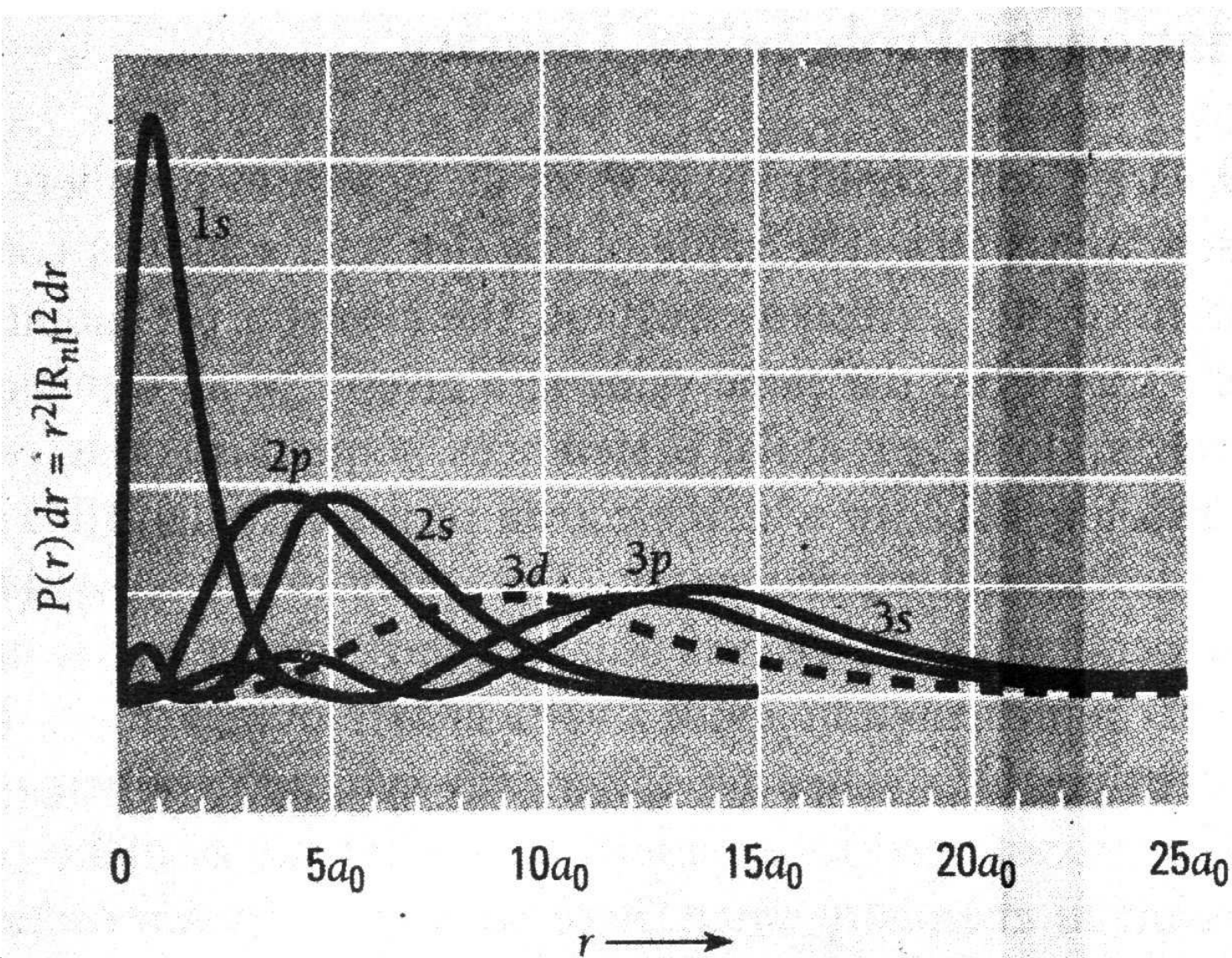
a_o —Bohr radius, $\mathcal{L}_{n+1}^{2\ell+1}$ — Associated Laguerre polys.

Radial Wave Functions





Radial Wave Functions – Probabilities





Radial Wave Functions - Key Points

- R_n^ℓ has $n - (\ell + 1)$ “nodes”! Roughly, this means that when n is large and ℓ is small, there is more energy in the radial degree of freedom
- At what radius $r_{n,\ell}^{max}$ is it most likely to find the particle? Turns out that, for a given n , $\ell = 0$ is the “outer most” and $\ell = n - 1$ are the “inner most”! Recall, f shells being called as “deep shells”!
- Most chemistry is due to this! For example, this is why transition metals are very happy to part with their s -electrons!



Complete Wavefunctions

- The full wave functions for H-atom are

$$\langle r, \theta, \phi | n, l, m \rangle = R_n^\ell(r) Y_\ell^m(\theta, \phi)$$

- We are more familiar with s, p, d, f orbitals, how are they related to the full wave functions?
- Let us look at some specific cases



Complete Wavefunctions

Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2$, and 3^*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

Orbitals!

- Key idea: Any linear combination of degenerate energy states is also an energy state
- Useful to create orthogonal states with symmetries that reflect the "crystalline" environment
- *s*-orbitals: $|1s\rangle = |1, 0, 0\rangle$
- *p*-orbitals: $|2p_z\rangle = |2, 1, 0\rangle$, $|2p_x\rangle = \frac{|2,1,1\rangle + |2,1,-1\rangle}{\sqrt{2}}$ and $|2p_y\rangle = \frac{|2,1,1\rangle - |2,1,-1\rangle}{\sqrt{2}i}$
- *d*-orbitals: $|3d_{3z^2-r^2}\rangle = |3, 2, 0\rangle$, $|3d_{xz}\rangle = \frac{|3,2,1\rangle + |3,2,-1\rangle}{\sqrt{2}}$, $|3d_{yz}\rangle = \frac{|3,2,1\rangle - |3,2,-1\rangle}{\sqrt{2}i}$, $|3d_{x^2-y^2}\rangle = \frac{|3,2,2\rangle + |3,2,-2\rangle}{\sqrt{2}}$, $|3d_{xy}\rangle = \frac{|3,2,2\rangle - |3,2,-2\rangle}{\sqrt{2}i}$

Can understand things like crystal field splitting from this



Structure of Multi-Electron Atoms

Need to take care of the following things

- Spin!
- Pauli's Principle
- Coulomb interactions (+ spin $\sim$ Hund's Rule)
- Spin-orbit Coupling
- Even relativistic effects, sometimes!
- Angular momentum states no longer degenerate (Aufbau principle)
- Gives rise to the material "music"