Lec #20: 7 OCT 11

LAST TIME: Hydrogen Spectrum and Bohr Atom

TODAY: Atomic *Transitions*

- Modifications required for >1 electron
- Atomic Structure
- Selection Rules; Atomic "Terms"
- Measuring Line Strength

NEXT: Line Strength and Line Profiles

- Calculating Line Luminosity
- Bound-Bound Rate Coefficients
- Broadening Mechanisms

Important QM Fundamentals

- Classical physics breaks down on the size scale of atoms, but the following are still conserved
  - mass-energy
  - momentum
  - angular momentum
  - charge
- Heisenberg Uncertainty Principle
  - h-bar serves as a quantum of "action" (E*t or p*x)
  - $\Delta p \Delta x \sim h_b$ and $\Delta E \Delta t \sim h_b$
  - for an atom $\Delta x \sim \lambda_D$ --> electron "clouds"

- Schrödinger equation
  - $H\psi = E\psi$
  - H is Hamiltonian operator(T+U)
  - E are Energy eigenvalues
  - ψ is "wave function" describing probability of finding electron in a particular "state"

    $\{h_b^2/2m\sum\nabla_j^2 + E + Ze^2 \sum 1/r_j - \sum e^2/r_{ij}\}\ \psi = 0$
  - electron K.E.; E; nuclear potential; e-e potential
  - Simplifications: time-independent, central-field (so angular momentum is constant)
  - $\psi(r,\theta,\varphi)$ then separable
    - radial part: R_{nl} (requires 2 quantum #'s)
    - angular part: P_l^m (requires a 3rd quantum #)

- Relativistic solution (Dirac equation) introduces a 4th quantum # (spin)
- Pauli Exclusion Principle: no 2 particles with half-integer (times h-bar) spin angular momentum ("fermions") can exist in the same state; not a problem for problem for particles with integer spin ("bosons")
- With all of this information, it is now possible for us to construct multi-electron atoms and understand the periodic table...

Electron Configuraton

- Quantum numbers: $n\ \ l\ \ m_l\ \ m_s$
  - n = "principal" 1, 2, 3, ...
  - l = "orbital a.m." 0, 1, ... , n-1
  - m_l = "magnetic moment" $-l, -l+1, \ldots, l-1, l$
  - m_s = "spin" -1/2 or +1/2
- $j = l + m_s$ = total angular momentum
- "configuration" nl_j^x

n	shell		l	
1	K		0	s "sharp"
2	L		1	p "principal"
3	M		2	d "diffuse"
4	N		3	f "fundamental"

DEGENERACY

- degenerate states in a single-electron atom:
  - for each n, there are $2n^2$ "degenerate" states
  - for each l, there are $2(2l+1)$ "degenerate" states
- degeneracy removed by multi-electron interactions ("spin-orbit coupling"), external magnetic fields, nuclear spin, etc.
- let's practice building atoms according to these rules....

TABLE 7-1

Quantum States of Successive Electrons

Electron	Energy Level n	Angular Momentum l	Designation	Magnetic Moment m	Spin	Shell
1st	1	0	1*s*	0	$-\frac{1}{2}$	*K*
2nd	1	0	1*s*	0	$\frac{1}{2}$	*K*
3rd	2	0	2*s*	0	$-\frac{1}{2}$	L_1
4th	2	0	2*s*	0	$\frac{1}{2}$	L_1
5th	2	1	2*p*	−1	$-\frac{1}{2}$	L_2
6th	2	1	2*p*	−1	$\frac{1}{2}$	L_2
7th	2	1	2*p*	0	$-\frac{1}{2}$	L_2
8th	2	1	2*p*	0	$\frac{1}{2}$	L_2
9th	2	1	2*p*	1	$-\frac{1}{2}$	L_2
10th	2	1	2*p*	1	$\frac{1}{2}$	L_2
11th	3	0	3*s*	0	$-\frac{1}{2}$	M_1
12th	3	0	3*s*	0	$\frac{1}{2}$	M_1
13th	3	1	3*p*	−1	$-\frac{1}{2}$	M_2
14th	3	1	3*p*	−1	$\frac{1}{2}$	M_2
15th	3	1	3*p*	0	$-\frac{1}{2}$	M_2
16th	3	1	3*p*	0	$\frac{1}{2}$	M_2
17th	3	1	3*p*	1	$-\frac{1}{2}$	M_2
18th	3	1	3*p*	1	$\frac{1}{2}$	M_2
19th	4	0	4*s*	0	$-\frac{1}{2}$	N_1
20th	4	0	4*s*	0	$\frac{1}{2}$	N_1
21st	3	2	3*d*	−2	$-\frac{1}{2}$	M_3
22nd	3	2	3*d*	−2	$\frac{1}{2}$	M_3
etc.						

Table 9.1

Neutral atoms

Atom	Z	K 1s	L 2s	L 2p	M 3s	M 3p	M 3d	N 4s	N 4p	N 4d	O 5s	Ground level
H	1	1										$^2S_{1/2}$
He	2	2										$^1S_0$
Li	3	2	1									$^2S_{1/2}$
Be	4	2	2									$^1S_0$
B	5	2	2	1								$^2P^o_{1/2}$
C	6	2	2	2								$^3P_0$
N	7	2	2	3								$^4S^o_{3/2}$
O	8	2	2	4								$^3P_2$
F	9	2	2	5								$^2P^o_{3/2}$
Ne	10	2	2	6								$^1S_0$
Na	11	2	2	6	1							$^2S_{1/2}$
Mg	12				2							$^1S_0$
Al	13				2	1						$^2P^o_{1/2}$
Si	14		10		2	2						$^3P_0$
P	15				2	3						$^4S^o_{3/2}$
S	16		Ne core		2	4						$^3P_2$
Cl	17				2	5						$^2P^o_{3/2}$
Ar	18				2	6						$^1S_0$
K	19	2	2	6	2	6		1				$^2S_{1/2}$
Ca	20							2				$^1S_0$
Sc	21						1	2				$^2D_{3/2}$
Ti	22						2	2				$^3F_2$
V	23			18			3	2				$^4F_{3/2}$
Cr	24						5	1				$^7S_3$
Mn	25			A core			5	2				$^6S_{5/2}$
Fe	26						6	2				$^5D_4$
Co	27						7	2				$^4F_{9/2}$
Ni	28						8	2				$^3F_4$
Cu	29	2	2	6	2	6	10	1				$^2S_{1/2}$
Zn	30							2				$^1S_0$
Ga	31							2	1			$^2P^o_{1/2}$
Ge	32				28			2	2			$^3P_0$
As	33							2	3			$^4S^o_{3/2}$
Se	34							2	4			$^3P_2$
Br	35							2	5			$^2P^o_{3/2}$
Kr	36							2	6			$^1S_0$
Rb	37	2	2	6	2	6	10	2	6		1	$^2S_{1/2}$
Sr	38										2	$^1S_0$
Y	39									1	2	$^2D_{3/2}$
Zr	40									2	2	$^3F_2$
Nb	41					36				4	1	$^6D_{1/2}$
Mo	42									5	1	$^7S_3$
Tc	43					Kr core				5	2	$^6S_{5/2}$
Ru	44									7	1	$^5F_5$
Rh	45									8	1	$^4F_{9/2}$
Pd	46									10		$^1S_0$

Atom	Z	K L M N (K 1s, L 2s 2p, M 3s 3p 3d, N 4s 4p 4d) 46 Pd core	N 4f	O 5s	O 5p	O 5d	O 5f	P 6s	P 6p	P 6d	Q 7s	Ground level
Ag	47			1								$^2S_{1/2}$
Cd	48			2								$^1S_0$
In	49			2	1							$^2P^o_{1/2}$
Sn	50			2	2							$^3P_0$
Sb	51			2	3							$^4S^o_{3/2}$
Te	52			2	4							$^3P_2$
I	53			2	5							$^2P^o_{3/2}$
Xe	54			2	6							$^1S_0$
Cs	55			2	6			1				$^2S_{1/2}$
Ba	56			8				2				$^1S_0$
La	57					1		2				$^2D_{3/2}$
Ce	58		1	2	6	1		2				[illegible]
Pr	59		3					2				$^4I^o_{9/2}$
Nd	60		4					2				$^5I_4$
Pm	61		5					2				$^6H^o_{5/2}$
Sm	62		6					2				$^7F_0$
Eu	63		7					2				$^8S^o_{7/2}$
Gd	64		7	8		1		2				$^9D_2$
Tb	65		9					2				$^6H^o_{15/2}$
Dy	66		10					2				$^5I_8$
Ho	67		11					2				$^4I^o_{15/2}$
Er	68		12					2				$^3H_6$
Tm	69		13					2				$^2F^o_{7/2}$
Yb	70		14					2				$^1S_0$
Lu	71		14			1		2				$^2D_{3/2}$
Hf	72		14	2	6	2		2				$^3F_2$
Ta	73					3		2				$^4F_{3/2}$
W	74					4		2				$^5D_0$
Re	75		46+22			5		2				$^6S_{5/2}$
Os	76					6		2				$^5D_4$
Ir	77					7		2				$^4F_{9/2}$
Pt	78					9		1				$^3D_3$
Au	79		14	2	6	10		1				$^2S_{1/2}$
Hg	80							2				$^1S_0$
Tl	81							2	1			$^2P^o_{1/2}$
Pb	82		46+32					2	2			$^3P_0$
Bi	83							2	3			$^4S^o_{3/2}$
Po	84							2	4			$^3P_2$
At	85							2	5			$^2P^o_{3/2}$
Rn	86							2	6			$^1S_0$
Fr	87		14	2	6	10		2	6		1	$^2S_{1/2}$
Ra	88										2	$^1S_0$
Ac	89		46+32							1	2	$^2D_{3/2}$
Th	90									2	2	$^3F_2$
Pa	91						2			1	2	$^4K_{11/2}$
U	92						3			1	2	$^5L^o_6$

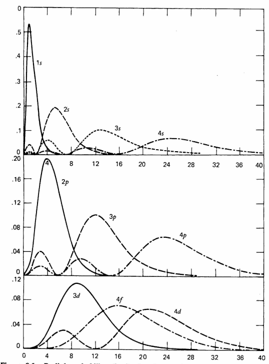

Figure 9.1 Radial probability distribution for an electron in several of the lowest levels of hydrogen. The abscissa is the radius in atomic units. (Taken from Condon, E. and Shortley, G. 1963, The Theory of Atomic Spectra, Cambridge, Cambridge University Press.)

Which Transitions are Possible?

- Well, almost all of them CAN happen, but the rates break them into "*allowed*" and "*forbidden*"
- Δl=1 : photon carries integer spin, so any transition involving a photon must also involve a change in angular momentum of precisely h-bar!
- Δm_l = -1, 0, or 1
- These two "selection rules" fully specify hydrogenic atoms, but much more happens in multi-electron atoms