Many Electron Atom Ch. 8

or, taking the "mystery" out of Chem-mystery

The many electron atom

Let's be completely general, can consider a neutral atom with Z protons and Z electrons in "orbit". ($m_N >> m_e$)

The SE for this system is:

$$V(r_i) = \frac{Ze^2}{4\pi\varepsilon_0 |\vec{x}_i|}$$

$$-\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\nabla_i^2\,\Psi(\vec{x}_1,\dots,\vec{x}_Z) - \sum_{i=1}^{Z} V(r_i)\,\Psi(\vec{x}_1,\dots\vec{x}_Z)$$

$\frac{\hbar^2}{2m}$: ↑ electron mass

$\Psi(\vec{x}_1,\dots,\vec{x}_Z)$: many particle e⁻ wave fn

$\sum_{i=1}^{Z} V(r_i)\,\Psi(\vec{x}_1,\dots\vec{x}_Z)$: attractive force between the nucleus and the electrons

(1)

$$+\left(\frac{1}{2}\right)\sum_{i=1}^{Z}\sum_{\substack{j=1\\ i\neq j}}^{Z} V_{ij}(|\vec{x}_i-\vec{x}_j|)\,\Psi(\vec{x}_1\dots\vec{x}_Z) = E_i\,\Psi(\vec{x}_1,\dots\vec{x}_Z)$$

$\left(\frac{1}{2}\right)$: ↑ don't overcount

$\sum_{\substack{j=1\\ i\neq j}}^{Z}$: ↑ don't count itself

$V_{ij}(|\vec{x}_i-\vec{x}_j|)$: ↑ $\frac{e^2}{4\pi\varepsilon_0|\vec{x}_i-\vec{x}_j|}$

$E_i\,\Psi(\vec{x}_1,\dots\vec{x}_Z)$: ↑ total energy, assuming the atom is at rest

$\sum_{i=1}^{Z}\sum_{\substack{j=1\\ i\neq j}}^{Z} V_{ij}(|\vec{x}_i-\vec{x}_j|)\,\Psi(\vec{x}_1\dots\vec{x}_Z)$: Repulsive force of each of the electrons on each other

It probably wouldn't suprise you that this can not be solved mathematically from first principles. [However, very good computer solutions are possible.]

A successful approach to solving this is to first solve it ignoring the repulsive term, i.e. $V_{ij}=0$, and in this approximation each individual e^- wave function is independent:

(2) $$\Psi(\vec{x}_1,\ldots\vec{x}_Z) = \prod_{i=1}^{Z}\psi(\vec{x}_i) = \psi(\vec{x}_1)\psi(\vec{x}_2)\cdots\psi(\vec{x}_Z)$$

where the $\psi(\vec{x}_i)$ are the hydrogenic wave functions we have been studying, and

(3) $$E_T = \sum_{i=1}^{Z} E_i$$ ← single hydrogenic atom energies

So, now let's assemble an atom from its constituent components, starting with a nucleus & a single electron, one by one...

Q. What would happen?

A. Each $\psi_{n,\ell,m_\ell}(\vec{x}_i) \rightarrow \psi_{100}(\vec{x}_i)$

would decay to the ground state!

We <u>know</u> experimentally, that this does <u>not</u> happen. Something else must be going on.

First, some facts of nature...

Fundamental & composite "particles" organize themselves into two general classes of particles

A) Fermions (named after Enrico) have half-integral spin, $1/2, 3/2, \ldots$

Fermion → leptons e.g. $e^{\pm}$ $\nu_{e^{\pm}}$, $\mu^{\pm}$, $\nu_{\mu^{\pm}}$, $\tau^{\pm}$, $\nu_{\tau^{\pm}}$

$e^{\pm}$: electron; $\mu^{\pm}$: muon; $\tau^{\pm}$: tauon

$\nu_{e^{\pm}}$, $\nu_{\mu^{\pm}}$, $\nu_{\tau^{\pm}}$: neutrinos

quarks, neutrons, protons, ^3He... : composites

The wave functions of many particle states must be anti-symmetric under the optical exchange of any two fermions

e.g. 2 particles

(4) $$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left\{ \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1) \right\}$$

note: the minus sign

a = set of quantum #'s associated with particle "a",

b = " particle "b"

Note that

(5) $$\Psi(\vec{x}_2, \vec{x}_1) = -\Psi(\vec{x}_1, \vec{x}_2)$$

This is very much like parity, but an even more abstract form of anti-symmetry

B) Bosons (Satyendra Nath Bose)

integral spin particles γ's, mesons, gluons, ^4He

These have positive interchange properties

e.g. 2 boson wave function

(6) $$\Psi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \left\{ \psi_a(\vec{x}_1)\psi_b(\vec{x}_2) + \psi_a(\vec{x}_2)\psi_b(\vec{x}_1) \right\}$$ (+ note)

(7) $$\Psi(\vec{x}_2, \vec{x}_1) = +\Psi(\vec{x}_1, \vec{x}_2)$$

Since electrons are Fermions, no two electrons can have identical quantum numbers in an atom. Because, if a=b in (4)

$$\Psi(\vec{x}_1, \vec{x}_2) = 0$$

This is called the

8.1 Pauli Exclusion Principle

"no two electrons can occupy the same quantum state (defined by the set of all quantum numbers)

For hydrogenic atoms

all e^- are $s = \frac{1}{2}$

e^- have quantum #s $\underbrace{n, l, m_l, s, m_s}$

defines the quantum state

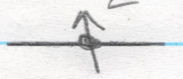
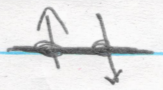
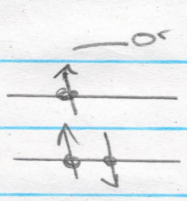
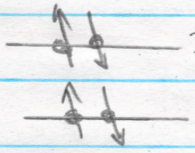
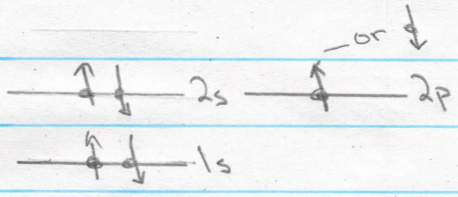
e^- state in an atom $|n l m_l m_s\rangle$ (s is always ½, so it's not expressed, but understood)

aside

- ^4He (boson) boils at 4.2°K
  is a superfluid at 2.17°K
- ^3He (fermion) boils at 3.2°K
  is a superfluid at ≈0.001°K!
  (formation of Cooper pairs)

OK, now with this new fact of nature, let's build an atom, noting that the e^- will always acquire the lowest energy possible.

↑ ⇒ e^- with $m_s = +\frac{1}{2}$ ↓ ⇒ e^- with $m_s = -\frac{1}{2}$

Z			spectroscopic notation
1	H	 1s ($n=1, l=0, m_l=0, m_s = +\frac{1}{2}$ or $\frac{1}{2}$)	$1s^1$
2	He	 1s ($n=1, l=0, m_l=0, m_s = \pm\frac{1}{2}$)	$[1s^2]$ Closed shell
3	Li	 2s ($n=2, l=0, m_l=0, m_s = +\frac{1}{2}$ or $-\frac{1}{2}$); 1s ($n=1, l=0, m_l=0, m_s = \pm\frac{1}{2}$)	$1s^2 2s^1$ or $[He]2s^1$
4	Be	 2s ($n=2, l=0, m_l=0, m_s = \pm\frac{1}{2}$); 1s ($n=1, l=0, m_l=0, m_s = \pm\frac{1}{2}$)	$1s^2 2s^2$ or $[He]2s^2$
5	B	 2s, 2p, 1s	$1s^2 2s^2 2p^1$ or $[He]2p^1$ $2s^2$
6	C		$[He]2p^2$
7	N		$[He]2p^3$
8	O		$[He]2p^4$
9	F		$[He]2p^5$
10	Ne		$[He]2p^6$ closed n=2 shell
11	Na		$[Ne]3s^1$

and so on

The electron repulsion potential does have a profound effect on the order in which the levels are filled. The filling order has been observed experimentally and a "rule" formulated by Madelung (1936)

a) Orbitals are filled in order of increasing $n+l$. [Since $n\uparrow\ l\uparrow \Rightarrow$ less close to the nucleus, more screening; less binding]

b) When two orbitals have the same $n+l$, the lower n's get filled first

filling order	$n+l$	Closed shells
1s	1	[He]
2s	2	
2p	3	[Ne]
3s	3	
3p	4	[Ar]
4s	4	
3d	5	(Cu)-{Zn}
4p	5	[Kr]
5s	5	
4d	6	(Ag)-{Cd}
5p	6	[Xe]
6s	6	
4f	7	
5d	7	(Au)-{Hg}
6p	7	[Rn]
7s	7	
5f	8	
6d		
7p		

p=1
d=2
f=3
g=4

And this filling order is practically universal

The elements indicated by [ ] are the noble gases, and these are associated with the filling of the p shells.

Mini-shells, indicated by { } show some very interesting physical properties. (High ionization energies, meaning that the electrons are tightly bound)

So strong is this desire to fill the d-shells, that it produces 3 anomalies; the excellent conductors

		Electrical resistivity (nΩ·m)
Cu	$[Ar]4s^1 3d^{10}$	16.78
Ag	$[Kr]5s^1 4d^{10}$	15.89
Au	$[Xe]6s^1 5d^{10} 4f^{14}$	22.14

↑ conducting electrons

Al 28.2

Pt 105

Other good conductors Al $[Ne]3s^2 3p^1$

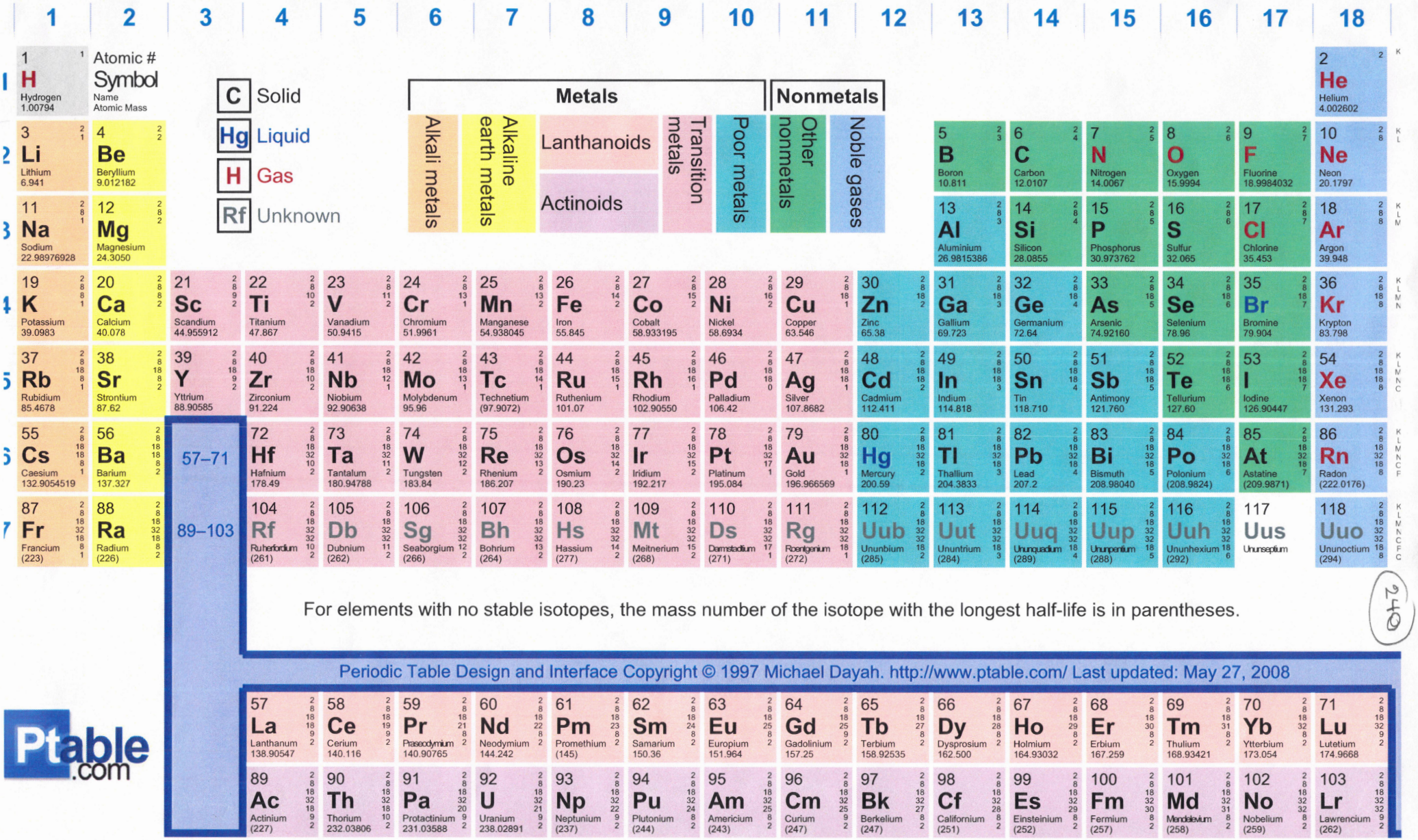
↑ conducting electron

Show periodic table

Show exceptions to Madelung's rule

- half-shell filling
- no really good explanation other than developing computer solutions to many-electron atoms

Periodic Table of Elements



For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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From Wiki...

electron configuration

Period 5			Period 6			Period 7		
Element	**Z**	**Electron Configuration**	**Element**	**Z**	**Electron Configuration**	**Element**	**Z**	**Electron Configuration**
Yttrium	39	[Kr] $5s^2\ 4d^1$	Lanthanum	57	[Xe] $6s^2\ 5d^1$	Actinium	89	[Rn] $7s^2\ 6d^1$
			Cerium	58	[Xe] $6s^2\ 4f^1\ 5d^1$	Thorium	90	[Rn] $7s^2\ 6d^2$
			Praseodymium	59	[Xe] $6s^2\ 4f^3$	Protactinium	91	[Rn] $7s^2\ 5f^2\ 6d^1$
			Neodymium	60	[Xe] $6s^2\ 4f^4$	Uranium	92	[Rn] $7s^2\ 5f^3\ 6d^1$
			Promethium	61	[Xe] $6s^2\ 4f^5$	Neptunium	93	[Rn] $7s^2\ 5f^4\ 6d^1$
			Samarium	62	[Xe] $6s^2\ 4f^6$	Plutonium	94	[Rn] $7s^2\ 5f^6$
			Europium	63	[Xe] $6s^2\ 4f^7$	Americium	95	[Rn] $7s^2\ 5f^7$
			Gadolinium	64	[Xe] $6s^2\ 4f^7\ 5d^1$	Curium	96	[Rn] $7s^2\ 5f^7\ 6d^1$
			Terbium	65	[Xe] $6s^2\ 4f^9$	Berkelium	97	[Rn] $7s^2\ 5f^9$
Zirconium	40	[Kr] $5s^2\ 4d^2$	Hafnium	72	[Xe] $6s^2\ 4f^{14}\ 5d^2$			
Niobium	41	[Kr] $5s^1\ 4d^4$	Tantalium	73	[Xe] $6s^2\ 4f^{14}\ 5d^3$			
Molybdenum	42	[Kr] $5s^1\ 4d^5$	Tungsten	74	[Xe] $6s^2\ 4f^{14}\ 5d^4$			
Technetium	43	[Kr] $5s^2\ 4d^5$	Rhenium	75	[Xe] $6s^2\ 4f^{14}\ 5d^5$			
Ruthenium	44	[Kr] $5s^1\ 4d^7$	Osmium	76	[Xe] $6s^2\ 4f^{14}\ 5d^6$			
Rhodium	45	[Kr] $5s^1\ 4d^8$	Iridium	77	[Xe] $6s^2\ 4f^{14}\ 5d^7$			
Palladium	46	[Kr] $4d^{10}$	Platinum	78	[Xe] $6s^1\ 4f^{14}\ 5d^9$			
Silver	47	[Kr] $5s^1\ 4d^{10}$	Gold	79	[Xe] $6s^1\ 4f^{14}\ 5d^{10}$			
Cadmium	48	[Kr] $5s^2\ 4d^{10}$	Mercury	80	[Xe] $6s^2\ 4f^{14}\ 5d^{10}$			

Transitions

Atoms in an excited states – at least one electron is in a higher state, than it's ground state.

Krane p. 251 "Decay transitions follow the $\Delta l = \pm 1$ selection rule".

?

What does this mean and why?

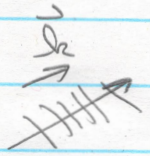
Photons result from these transitions, and photons are known to carry off "at least" one unit of angular momentum, since the photon's intrinsic spin is $S_\gamma = 1\hbar$ (one unit)

Mathematically, the dominant transition for γ-decay is the $\vec{x}$ transition we have been mentioning throughout the course. The $\vec{x}$ transition is also called the dipole transition.

How does this arise?

The photon wave function has the form

$$\psi_\gamma = N_\gamma e^{i\vec{k}\cdot\vec{x}}$$



The transition rate is

$$\lambda \propto |M_{fi}|^2$$

where $M_{fi} = \langle n_f l_f m_{sf} | e^{i\vec{k}\cdot\vec{x}} | n_i l_i m_{si} \rangle$ ← quns describing the initial state

$$= \langle n_f l_f m_{sf} | 1 + i\vec{k}\cdot\vec{x} + (O(\vec{k}\cdot\vec{x})^2) \cdot | n_i l_i m_{si} \rangle$$

$$\simeq i\vec{k} \cdot \langle n_f l_f m_{sf} | \vec{x} | n_i l_i m_{si} \rangle$$

since $\langle f | i \rangle = 0$ if $f \neq i$

$\langle \vec{x}^2 \rangle << \langle \vec{x} \rangle$ (less overlap of wavefns)

See page 307 in Krane

$$Y_{1\pm1} = \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin\theta\, e^{\pm i\phi}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$\vec{x} = \left(\hat{x}\sin\theta\cos\phi + \hat{y}\sin\theta\sin\phi + \hat{z}\cos\theta\right) r$$

$$= \frac{\sqrt{4\pi}}{3}\left\{ \frac{Y_{11} + Y_{1-1}}{\sqrt{2}}\hat{x} + \frac{Y_{11} - Y_{1-1}}{i\sqrt{2}}\hat{y} + Y_{10}\hat{z} \right\}$$

Let's assume, for the sake of simplicity that

$$\vec{k} = k\hat{z}$$

Then $m_{fi} = \langle n_f l_f | r | n_i l_i \rangle \sqrt{\frac{4\pi}{3}} \int d\Omega\, Y^*_{l_f m_f} Y_{10} Y_{l_i m_i}$

$= \langle n_f l_f | r | n_i l_i \rangle \sqrt{\frac{4\pi}{3}} \int d\Omega\, Y^*_{l_f m_i} Y_{10} Y_{l_i m_i}$

i.e. $m_f = m_i$

and $\int d\Omega\, Y^*_{l_f m_i} Y_{10} Y_{l_i m_i} = 0$ unless

$l_f = l_i \pm 1$

(just math)

(same conclusion for any direction)

So $m_{fi} = C \langle n_f (l_i \pm 1) | r | n_i l_i \rangle$ (C: same constant)

$\neq 0$ for any l_i, n_f, n_i

That's where the $\Delta l = \pm 1$ transition rule comes from

Other Δl's are possible but much less probable.

(NERS 312 topic)

Coupling spins

Sometimes $\vec{l}$ is not measurable, nor is $\vec{s}$ because they are very strongly coupled.

Note: In atomic physics they are weakly coupled
In nuclear " " " strongly "

However, total angular momentum is always conserved, and therefore, an observable.

The rules of observation are as follows

Total angular momentum for a single particle is called $\vec{j}$.

$$\vec{j} = \vec{l} + \vec{s} \qquad \langle J^2 \rangle = \hbar^2 j(j+1)$$

$$\langle J_z \rangle = \hbar m_j$$

$|l-s| \leq j \leq l+s$ (integral jumps)

$m_j \leq |j|$ integral jumps

example 1

An electron is in a p state ($\ell = 1$)
What are its possible j's, m_j's?

$$|\ell - s| \leq j \leq \ell + s$$

$$\Rightarrow \quad \tfrac{1}{2} \leq j \leq \tfrac{3}{2}$$

$\therefore$ there are 2 possible j's $\quad j = \tfrac{1}{2}, \; m_j = \pm\tfrac{1}{2}$
$j = \tfrac{3}{2}, \; m_j = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}$
} 6 states no change

example 2

$\vec{2} + \vec{\tfrac{1}{2}}$ } 10 fold degeneracy

$\Rightarrow$ d-state

$j = \tfrac{3}{2}, \; m_j = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}$
$j = \tfrac{5}{2}, \; m_j = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}, \pm\tfrac{5}{2}$
} 10

(coupling 2 orbital angular momenta)

$\vec{L} = \vec{l}_1 + \vec{l}_2$ — upper case for 2 or more

$\langle L^2 \rangle = \hbar^2 L(L+1)$

$\langle L_z \rangle = \hbar m_L$

$|l_1 - l_2| \leq L \leq l_1 + l_2$

e.g. $\vec{l}_1 = \vec{3}$; $\vec{l}_2 = \vec{2}$ $\quad d = 7 \times 5 = 35$

$1 \leq L \leq 5$

$L=1$	$m_L = 0, \pm 1$	3
$L=2$	$m_L = 0, \pm 1, \pm 2$	5
$L=3$	$m_L = 0, \pm 1, \pm 2, \pm 3$	7
$L=4$	$m_L = 0, \pm 1, \pm 2, \pm 3 \pm 4$	9
$L=5$	$m_L = 0, \pm 1, \pm 2, \pm 3 \pm 4, \pm 5$	11

35

Coupling 2 spins

$\vec{S} = \vec{s}_1 + \vec{s}_2$

$\langle S^2 \rangle = \hbar^2 S(S+1)$

$\langle S_z \rangle = \hbar m_S$

e.g. $\vec{\frac{1}{2}} + \vec{\frac{1}{2}}$

$S = 0 \quad m_S = 0$

$= 1 \quad m_S = 0, \pm 1$

Coupling many spins

$$\vec{S} = \sum_{i=1}^{N} \vec{s}_i$$

$$\vec{L} = \sum_{i=1}^{N} \vec{l}_i$$

$$\vec{J} = \vec{L} + \vec{S} = \sum_{i=1}^{N} (\vec{l}_i + \vec{s}_i) = \sum_{i=1}^{N} \vec{j}_i$$

just keep coupling 2 at a time

e.g.

$$\vec{S} = \vec{s}_1 + \vec{s}_2 + \vec{s}_3$$ } 6-fold

$$= \vec{S}_{12} + \vec{s}_3 = \vec{S}_{12}, \; m_s = \pm\tfrac{1}{2}$$ } same

$$= \vec{s}_1 + \vec{s}_{23} = \vec{s}_1, \; m_s = \pm\tfrac{1}{2}$$

$$\vec{s}_2 + \vec{s}_3 = \vec{s}_{23}, \; m_s = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}$$

$$\vec{S} = \vec{s}_{13}$$ } 6-fold

$$\vec{s}_1 + \vec{s}_3 = \vec{s}_{13}, \; m_s = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}$$

Coupling spins in many electron atoms

Hund's rule:

1) find maximum M_S consistent with Pauli Exclusion Principle, set $S = M_S$
2) for that S, find maximum M_L, set $L = M_L$.

Examples

He: $\vec{S} = \vec{\frac{1}{2}} + \vec{\frac{1}{2}}$

$M_{S,max} = 0$ (Pauli)

$\vec{L} = \vec{0} + \vec{0} = \vec{0}$ $\quad L = 0$

He: $L = 0$ $\quad S = 0$

Li: $Li = \underbrace{[He]}_{L=0,\,S=0} 2s^1 \Rightarrow \begin{matrix} L = 0 \\ S = \frac{1}{2} \end{matrix}$

Be: $Be = [He]2s^2 \Rightarrow \begin{matrix} L = 0 \\ S = 0 \end{matrix}$

B: $B = \underbrace{[He][2s^2]}_{\text{both closed}} 2p^1 \quad \begin{matrix} S = \frac{1}{2} \\ L = 1 \end{matrix}$

C: $C = [1s^2][2s^2]2p^2$

$M_{S\,max} = 1$

$M_{L\,max} = 1$

$S = 1, L = 1$

N: $N = [1s^2][2s^2]2p^3$

m_s $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$

m_L -1 0 1

$M_{S\,MAX} = \frac{3}{2}$

$M_{L\,MAX} = 0$

$S = \frac{3}{2}, L = 0$

O: $O = [1s^2][2s^2]2p^4$

m_s $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $-\frac{1}{2}$

m_ℓ -1 0 1 1

$m_{S,MAX} = 1$

$m_{L,max} = 1$

$S = 1, L = 1$

F: $F = [1s^2][2s^2]2p^5$

m_s 1 1 0 0 -1

$m_{S,MAX} = \frac{1}{2}$

$m_{L,MAX} = 1$

$S = \frac{1}{2}, L = 1$

Ne: $Ne = [1s^2][2s^2][2p^6]$ $S = 0, L = 0$

all closed

Lasers (Light Amplification by Stimulated Emission of Radiation)

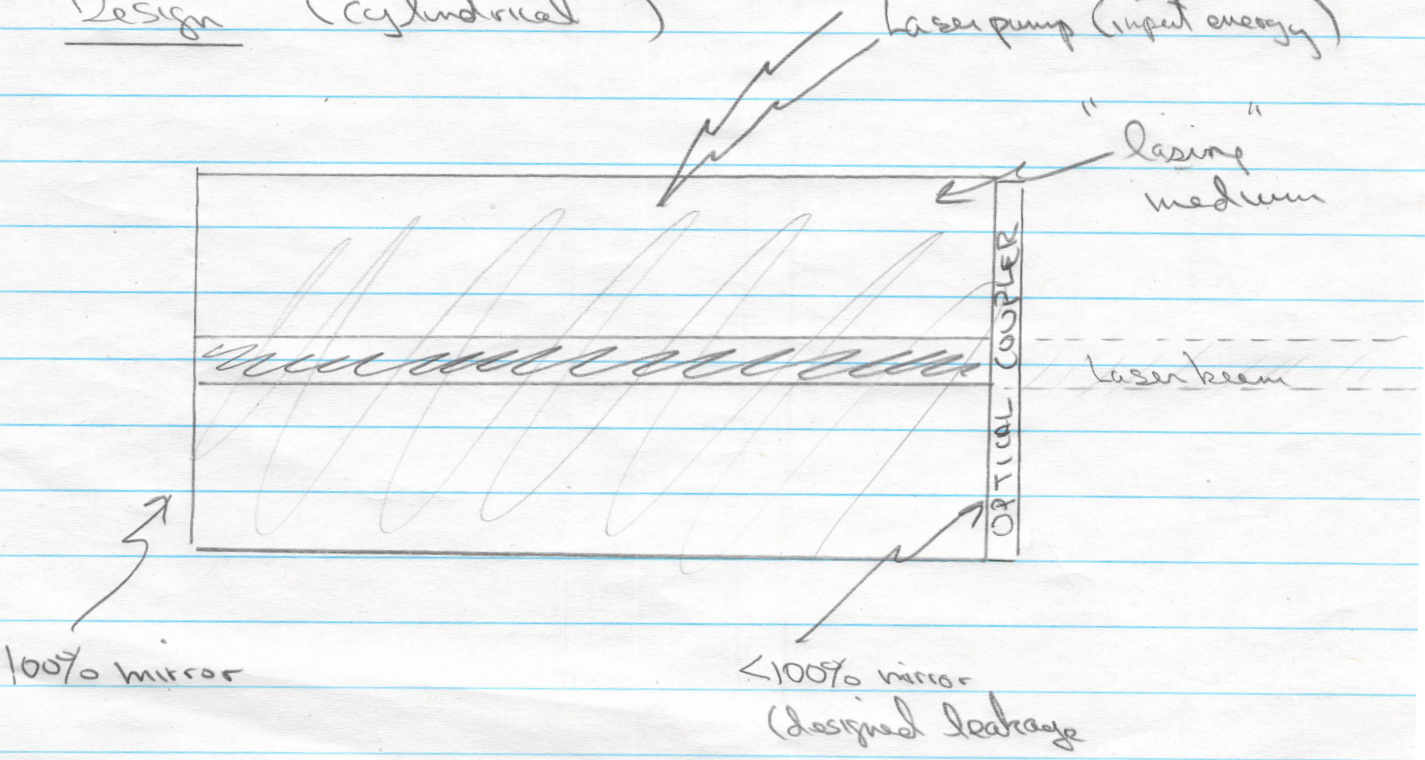
A source of mono energetic, coherent light

mono-energetic one energy

coherent monodirectional

peaks and troughs of all wavefunctions are aligned

Design (cylindrical)



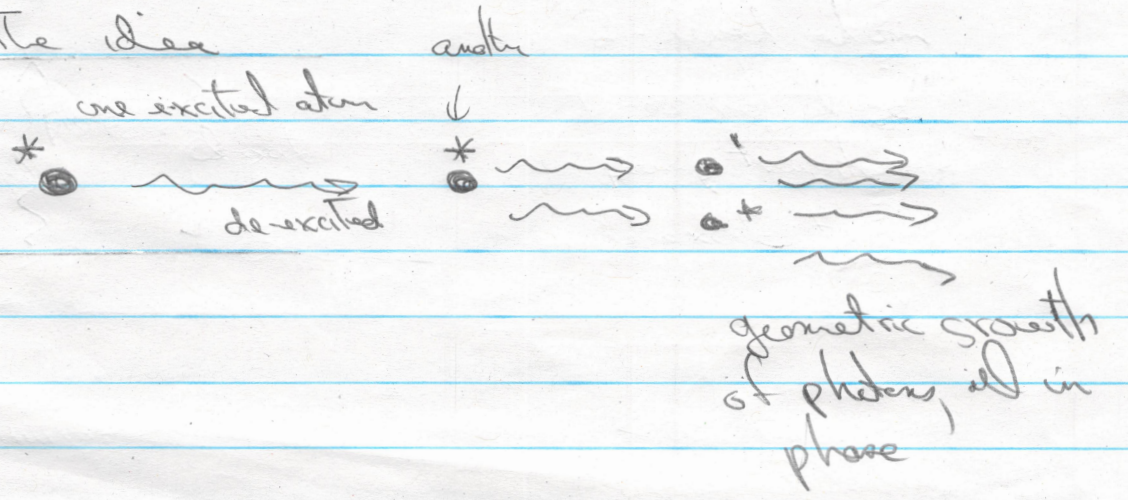
laser pump	electrical discharge, current, incoherent light source
"lasing" medium	or amplification medium (where the quantum mechanical magic happens) (later)
100% mirror	reflects all light, can also focus stray beams
<100% mirror	designed to reflect almost all the light, but allows some controlled leakage into the optical coupler
optical coupler	lens

Basically a "machine" for converting disorganized energy (pump energy) into organized energy, the laser beam.

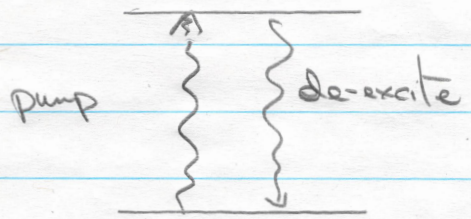
All the "magic" happens in the lasing material (gas, liquid, solid or plasma)

The amplification process

The idea

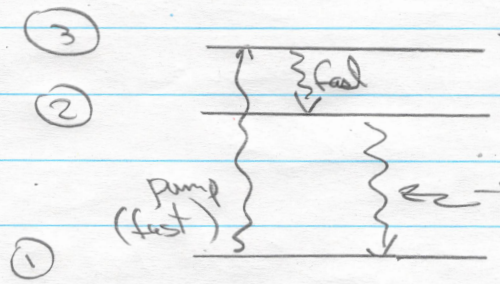


a 2-level atom

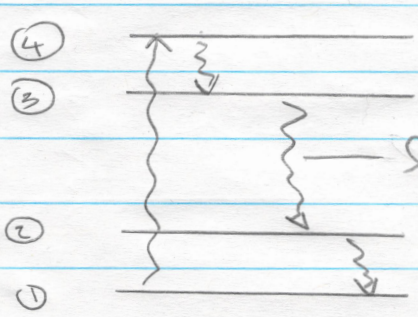


- does not "lase", because the pump & de-excitation processes are in direct competition, no amplification, the medium absorbs the lasing photons, also, pumping depopulates the ground state

a 3-level atom



This system can lase but is not ideal, There is "population inversion, more atoms at (2) rather than (1), but de-excitation decreases (2) and adds to (1), reducing the inversion



ideal system large population inversions

A practical example of a 4 level laser

