

8. Many-electron atoms

In this chapter we shall discuss :

- The Schrödinger equation for many-electron atoms
- The Pauli Exclusion Principle
- Electronic States in Many-Electron Atoms
- The Periodic Table
- Properties of the Elements
- Transitions revisited
- Addition of Angular Momenta
- Lasers

Introduction ...

To be completely general, consider a neutral atom with Z protons and Z electrons in “orbit”. The mass of the nucleus is assumed to be much, much larger than the mass of the electron ($m_N \gg m_e$).

The Schrödinger equation for this system is:

$$-\frac{\hbar^2}{2m_e} \sum_{i=1}^Z \nabla_i^2 U(\vec{x}_1, \dots, \vec{x}_Z) + \sum_{i=1}^Z V(r_i) U(\vec{x}_1, \dots, \vec{x}_Z) + \frac{1}{2} \sum_{i=1}^Z \sum_{\substack{j=1 \\ i \neq j}}^Z V(|\vec{x}_i - \vec{x}_j|) U(\vec{x}_1, \dots, \vec{x}_Z) = E_T U(\vec{x}_1, \dots, \vec{x}_Z) , \quad (8.1)$$

where $U(\vec{x}_1, \dots, \vec{x}_Z)$ is the many-electron wavefunction, and E_T is the total energy of the system, assuming that the center of mass of the atom is at rest.

- The first term, $-\frac{\hbar^2}{2m_e} \sum_{i=1}^Z \nabla_i^2 U(\vec{x}_1, \dots, \vec{x}_Z)$, is the total kinetic energy of the system.
- The second term term, $\sum_{i=1}^Z V(r_i) U(\vec{x}_1, \dots, \vec{x}_Z)$ is the attractive potential each electron feels from the nucleus, *viz.* $V(r_i) = \frac{-Ze^2}{4\pi\epsilon_0 r_i}$.
- The third term term, $\frac{1}{2} \sum_{i=1}^Z \sum_{\substack{j=1 \\ i \neq j}}^Z V(|\vec{x}_i - \vec{x}_j|) U(\vec{x}_1, \dots, \vec{x}_Z)$ is the repulsive potential that each electron feels all the other electrons, *viz.* $V(|\vec{x}_i - \vec{x}_j|) = \frac{e^2}{4\pi\epsilon_0 |\vec{x}_i - \vec{x}_j|}$.

... Introduction ...

Note that the $i \neq j$ means that each electron does not feel its own potential. Also, the factor of $\frac{1}{2}$ avoids double counting.

It probably wouldn't surprise you that this cannot be solved mathematically from the first principles (although some very good numerical solutions are possible).

A moderately successful approach to solving this is to first neglect the repulsive term (i.e. $V_{ij} = 0$) and to approximate each individual electron wavefunction as being independent:

$$U(\vec{x}_1, \dots, \vec{x}_Z) = \prod_{i=1}^Z u(\vec{x}_i) = u(\vec{x}_1)u(\vec{x}_2) \cdots u(\vec{x}_Z) , \quad (8.2)$$

where the $u(\vec{x}_i)$ are the hydrogenic wavefunctions we have been studying.

In this approximation

$$E_T = \sum_{i=1}^Z E_i , \quad (8.3)$$

where the E_i are the hydrogenic energies from the last chapter.

The Pauli Exclusion Principle (a.k.a. PEP) ...

Let's try a *gedanken* experiment¹ ... knowing only what we have learned, let's take a nucleus with Z protons and start adding electrons one at a time.

Whatever energy level the electron enters at, all electrons will then, by the second law of quantum thermodynamics (the principle of least energy), eventually go to the ground state. That is to say, no matter how $|nlm_l m_s\rangle$ starts off for each electron, it will always end up at $|100m_s\rangle$.

Nature does not work that way! Something else is going on.

First, some facts of Nature ...

Fundamental and composite “particles” are organized into only two general classes: **Fermions** and **Bosons**.

¹The phrase “gedanken experiment” means a “thought experiment”. Albert Einstein was very much enamored of its use.

... The Pauli Exclusion Principle ...

Fermions (named for Enrico Fermi) have half-integral spins, $\frac{1}{2}, \frac{3}{2}, \dots$

The known fundamental fermions are classified into two types,

type	generation	symbol	name	interactions
lepton	1 st	e^-/e^+	electron/positron	electromagnetic, weak, gravity
"	"	$\tilde{\nu}_e/\nu_e$	electron neutrinos	weak, gravity
"	2 nd	μ^-/μ^+	mus or muons	electromagnetic, weak, gravity
"	"	$\tilde{\nu}_\mu/\nu_\mu$	muon neutrinos	weak, gravity
"	3 rd	τ^-/τ^+	taus or tauon	electromagnetic, weak, gravity
"	"	$\tilde{\nu}_\tau/\nu_\tau$	tauon neutrinos	weak, gravity
quark	1 st	$u/\tilde{u}$	up	strong, electromagnetic, weak, gravity
"	"	$d/\tilde{d}$	down	strong, electromagnetic, weak, gravity
"	2 nd	$s/\tilde{s}$	strange	strong, electromagnetic, weak, gravity
"	"	$c/\tilde{c}$	charm	strong, electromagnetic, weak, gravity
"	3 rd	$t/\tilde{t}$	top	strong, electromagnetic, weak, gravity
"	"	$b/\tilde{b}$	bottom	strong, electromagnetic, weak, gravity

The third column gives the symbols for the particle/antiparticle pair.

Some examples of composite fermions are:

proton ($p = [uud]$), neutron ($n = [udd]$), tritium (${}^3\text{H} = [pnn]$), He-3 (${}^3\text{He} = [ppn]$) $\dots$

... The Pauli Exclusion Principle ...

For identical fermions, the wavefunctions of many-particle systems must be anti-symmetric with the exchange of any two particles.

For a two-particle identical fermion system, consider fermion “1” with the set of quantum numbers $q(1)$, at $\vec{x}_1$ forming a composite wavefunction with fermion “2”, that has its own set of quantum numbers $q(2)$ (e.g. $[n, l, m_l, m_s]$, at position $\vec{x}_2$). The anti-symmetric wavefunction can be constructed as follows:

$$U_2^A ([q(1), \vec{x}_1], [q(2), \vec{x}_2]) = \frac{1}{\sqrt{2}} [u_{q(1)}(\vec{x}_1)u_{q(2)}(\vec{x}_2) - u_{q(1)}(\vec{x}_2)u_{q(2)}(\vec{x}_1)] \quad (8.4)$$

The notation is quite interesting.

$u_{q(1)}(\vec{x}_1)$ means the single-particle wavefunction of particle “1” with quantum numbers $q(1)$ at position $\vec{x}_1$.

Thus, by virtue of the anti-symmetry, interchanging particles means not only interchanging positions, it also means exchanging quantum numbers as well. This anti-symmetry has two interesting consequences:

- If $q(1) = q(2)$ (each set of quantum numbers is the same), or
- if $\vec{x}_1 = \vec{x}_2$ (the positions are the same)

the composite wave function does not exist. It is zero.

... The Pauli Exclusion Principle ...

This is seen directly from (8.4). Its complete properties are:

$$\begin{aligned}
 \text{i)} \quad U_2^A([q(2), \vec{x}_1], [q(1), \vec{x}_2]) &= -U^A([q(1), \vec{x}_1], [q(2), \vec{x}_2]) && \text{anti-symmetric under change of quantum numbers} \\
 \text{ii)} \quad U_2^A([q(1), \vec{x}_2], [q(2), \vec{x}_1]) &= -U^A([q(1), \vec{x}_1], [q(2), \vec{x}_2]) && \text{anti-symmetric under change of spatial position} \\
 \text{iii)} \quad U_2^A([q, \vec{x}_2], [q, \vec{x}_1]) &= 0 && \text{zero, when the quantum numbers are the same} \\
 \text{iv)} \quad U_2^A([q(1), \vec{x}], [q(2), \vec{x}]) &= 0 && \text{zero, when the positions are the same}
 \end{aligned} \tag{8.5}$$

Systems with N identical fermions have the same properties as 2-particle systems. The anti-symmetric wavefunction is constructed as follows:

$$U_N^A(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_{q(1)}(\vec{x}_1) & u_{q(2)}(\vec{x}_1) & \cdots & u_{q(N)}(\vec{x}_1) \\ u_{q(1)}(\vec{x}_2) & u_{q(2)}(\vec{x}_2) & \cdots & u_{q(N)}(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_{q(1)}(\vec{x}_N) & u_{q(2)}(\vec{x}_N) & \cdots & u_{q(N)}(\vec{x}_N) \end{vmatrix}. \tag{8.6}$$

The object between vertical bars is the “determinant”, from linear algebra.

The rules in (8.5) apply when any two particles are involved.

... The Pauli Exclusion Principle ...

Bosons (named for Satyendra Nath Bose) have integral spins, 0, 1, ...

The known fundamental bosons are intermediaries of the forces of nature:

name	symbol	spin	interactions
gluon	g	$s = 1, m_s = \pm 1$	strong
photon	γ	$s = 1, m_s = \pm 1$	electromagnetic
charged vector bosons	$W^\pm$	$s = 1$	weak inelastic scattering
neutral vector boson	Z^0	$s = 1$	weak elastic scattering
Higgs boson	H^0	$s = 0$	decays into $\gamma\gamma, \tau\tilde{\tau}, Z^0Z^0, W^+W^-$
graviton	G	$s = 2, m_s = \pm 2$	gravity (hypothetical)

Some examples of composite bosons are:

pion ($\pi^+ = [u\bar{d}]$), deuteron ($D = [np]$), α -particle ($\alpha = [npnp]$), ...

For identical bosons, the wavefunctions of many-particle systems must be symmetric with the exchange of any two particles.

... The Pauli Exclusion Principle ...

For a two-particle identical boson system, consider boson “1” with the set of quantum numbers $q(1)$, at $\vec{x}_1$ forming a composite wavefunction with boson “2”, that has its own set of quantum numbers $q(2)$ (e.g. $[n, l, m_l, m_s]$, at position $\vec{x}_2$). The symmetric wavefunction can be constructed as follows:

$$U_2^S([q(1), \vec{x}_1], [q(2), \vec{x}_2]) = \frac{1}{\sqrt{2}} [u_{q(1)}(\vec{x}_1)u_{q(2)}(\vec{x}_2) + u_{q(1)}(\vec{x}_2)u_{q(2)}(\vec{x}_1)] \quad (8.7)$$

Note that

$$\begin{aligned} \text{i)} \quad U_2^S([q(2), \vec{x}_1], [q(1), \vec{x}_2]) &= +U^S([q(1), \vec{x}_1], [q(2), \vec{x}_2]) && \text{symmetric under change of quantum numbers} \\ \text{ii)} \quad U_2^S([q(1), \vec{x}_2], [q(2), \vec{x}_1]) &= +U^S([q(1), \vec{x}_1], [q(2), \vec{x}_2]) && \text{symmetric under change of spatial position} \\ \text{iii)} \quad U_2^S([q, \vec{x}_2], [q, \vec{x}_1]) &\neq 0 && \text{not zero, when the quantum numbers are the same} \\ \text{iv)} \quad U_2^S([q(1), \vec{x}], [q(2), \vec{x}]) &\neq 0 && \text{not zero, when the positions are the same} \end{aligned} \quad (8.8)$$

Systems with N identical bosons have the same properties as 2-particle systems. The symmetric wavefunction is constructed as follows:

$$U_N^S(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} u_{q(1)}(\vec{x}_1) & u_{q(2)}(\vec{x}_1) & \cdots & u_{q(N)}(\vec{x}_1) \\ u_{q(1)}(\vec{x}_2) & u_{q(2)}(\vec{x}_2) & \cdots & u_{q(N)}(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_{q(1)}(\vec{x}_N) & u_{q(2)}(\vec{x}_N) & \cdots & u_{q(N)}(\vec{x}_N) \end{pmatrix}. \quad (8.9)$$

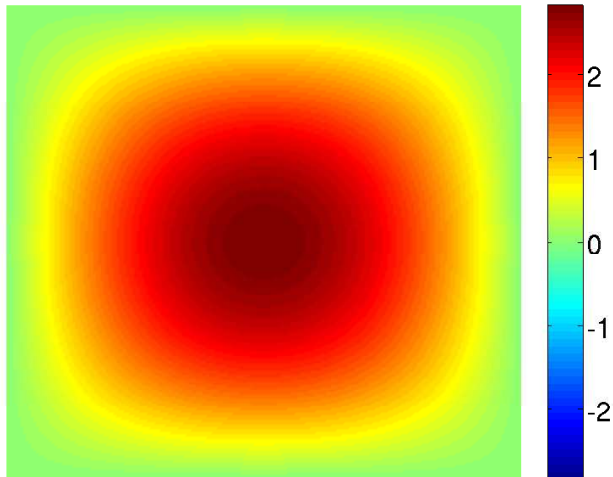
The object between the large parentheses is the “permanent”, from linear algebra.

The permanent is similar to the determinant, except all the negative signs are reversed.

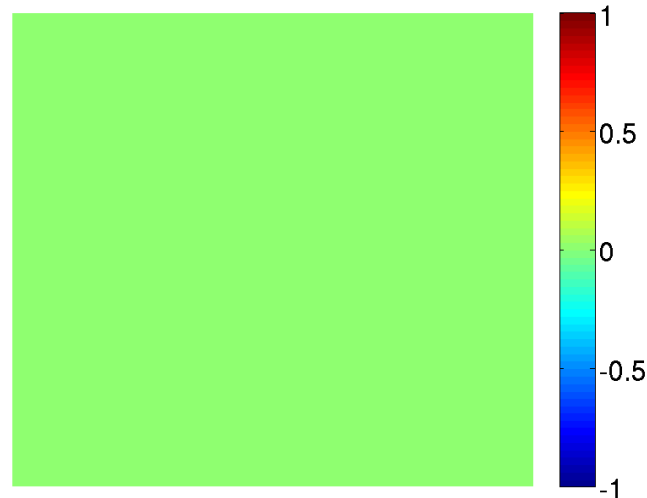
... The Pauli Exclusion Principle ...

Some examples of the probability amplitude for 2-particle systems:

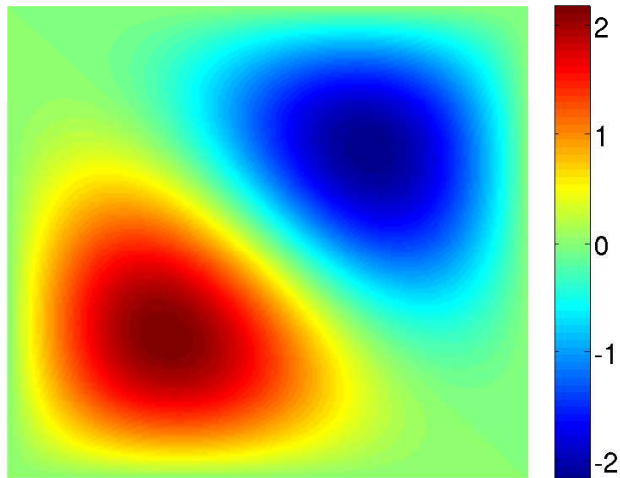
Two identical bosons (gs+gs) in a square well



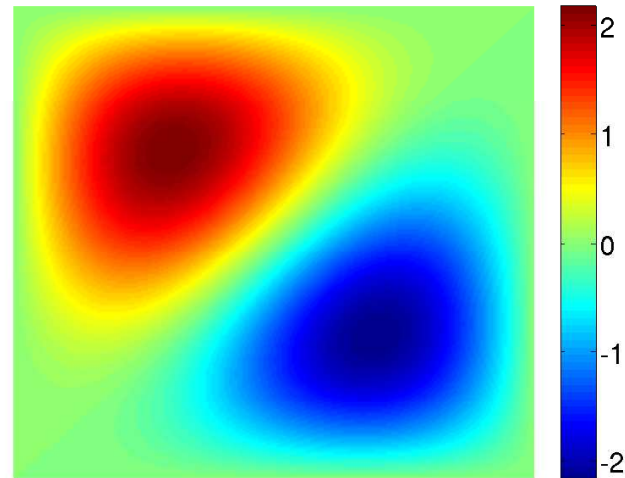
Two identical fermions (gs+gs) in a square well



Two identical bosons (gs+1st) in a square well



Two identical fermions (gs+1st) in a square well



... The Pauli Exclusion Principle ...

What is plotted on the previous page is:

$$\begin{array}{c|c|c|c} \text{(upper left)} & U_2^S([1, x_1], [1, x_2]) & \| & U_2^A([1, x_1], [1, x_2]) & \text{(upper right)} \\ \hline \text{(lower left)} & U_2^S([1, x_1], [2, x_2]) & \| & U_2^A([1, x_1], [2, x_2]) & \text{(lower right)} \end{array}$$

Observations:

- Due to the ∞ -wall boundary condition, the probability amplitude goes to zero at the boundaries. (green color)
- The upper right is all zero, because both fermions have the same quantum number. (all green)
- The lower right graph has a node along the the line $x_1 = x_2$, that goes from the lower left corner to the upper right. This is from property iv) in (8.5).

... The Pauli Exclusion Principle ...

The foregoing long introduction to the Pauli exclusion principle has revealed several things that are critical to the understanding of identical many-body systems.

The anti-symmetry behavior of identical fermions provides a precise mathematical form for the Pauli exclusion principle, which Pauli stated as:

“no two electrons can occupy the same quantum state” [defined as all the quantum numbers being exactly the same]

The mathematical development, however, provides a bonus! We see, for example, from the lower right hand corner figure of the previous page, that it “appears” that the two electrons are avoiding the line that makes their positions equal. It “looks like” there is a force, pushing them apart. However, it is just the anti-symmetry showing its effect.

We also see, that the upper left hand allows for two identical bosons to occupy the same regions of space with the same quantum numbers.

This phenomenon leads to very interesting phenomena ... superconductivity, superfluidity, and lasers. We shall discuss lasers later.

... The Pauli Exclusion Principle ...

For example,

X	statistics	$T_{\text{boiling}} [^{\circ}\text{K}]$	$T_{\text{superfluid}} [^{\circ}\text{K}]$
^4He	bosonic	4.7°	2.17°
^3He	fermionic	3.2°	$0.001^{\circ} !!!$

At low temperatures, the ^4He atoms, being bosons, coalesce into the ground state (this is called Bose-Einstein condensation) and are able to flow without friction.

^3He can do the same thing at ultra-low temperatures, where the fermions can pair up with each other and form composite bosons.

Superconductivity works the same way, but with electrons.

Electronic States in Many-Electron Atoms

Let's apply the PEP to filling the orbitals of neutral atoms.

Madelung's Rules ...

Repulsion by the electrons does have a profound effect on the order in which the levels are filled.

The filling order has been observed experimentally, and “rules” formulated by Madelung (1934). The rules are:

- a) Levels are filled in order of increasing $(n + l)$ [since $\uparrow n \uparrow l \Rightarrow$ more distance to the nucleus, more screening, less binding].
- b) When orbitals have the same $n + l$, the lower n is filled first.

		Orbitals			
		s	p	d	f
Principle Quantum Number (Energy Level, "n")	1	1s			
	2	2s	2p		
	3	3s	3p	3d	
	4	4s	4p	4d	4f
	5	5s	5p	5d	5f
	6	6s	6p	6d	6f
	7	7s	7p	7d	7f

Order: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

The ordering is given on the next page.

... Madelung's Rules ...

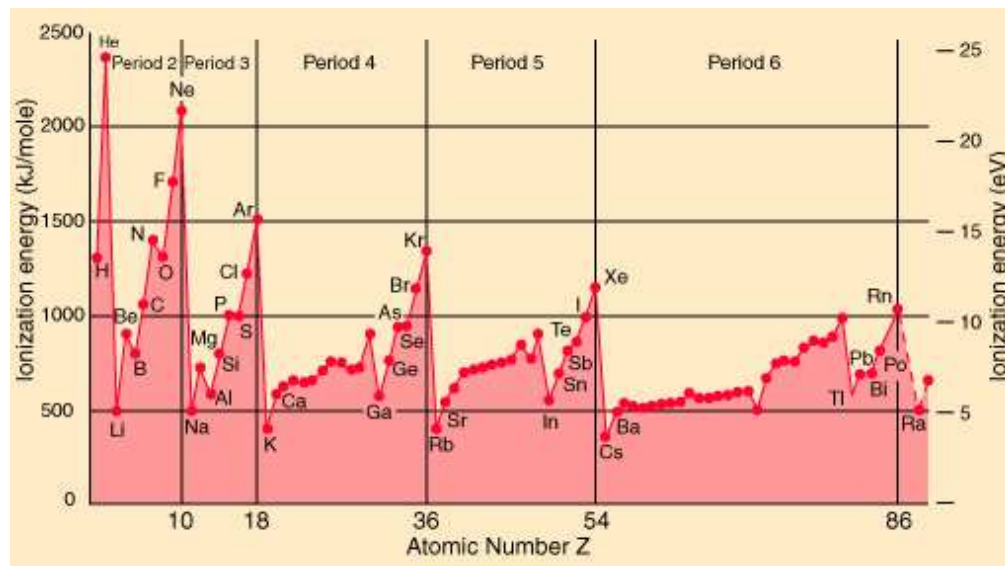
filling order	$n + l$	[Closed shells] & {Half-closed shells}	name
1s	1	[He]	Helium
2s	2		
2p	3	[Ne]	Neon
3s	3		
3p	4	[Ar]	Argon
4s	4		
3d	5	(Cu)—{Zn}	Copper — Zinc
4p	5	[Kr]	
5s	5		
4d	6	(Ag)—{Cd}	Silver — Cadmium
5p	6	[Xe]	
6s	6		
4f	7		
5d	7	(Au)—{Hg}	Gold — Mercury
6p	7	[Rn]	
7s	7	(Rg)—{Cn}	Roentgenium — Copernicium
5f	8	[Uno]	Ununoctium (temp)

Shell structure ...

This Madelung filling order is practically universal.

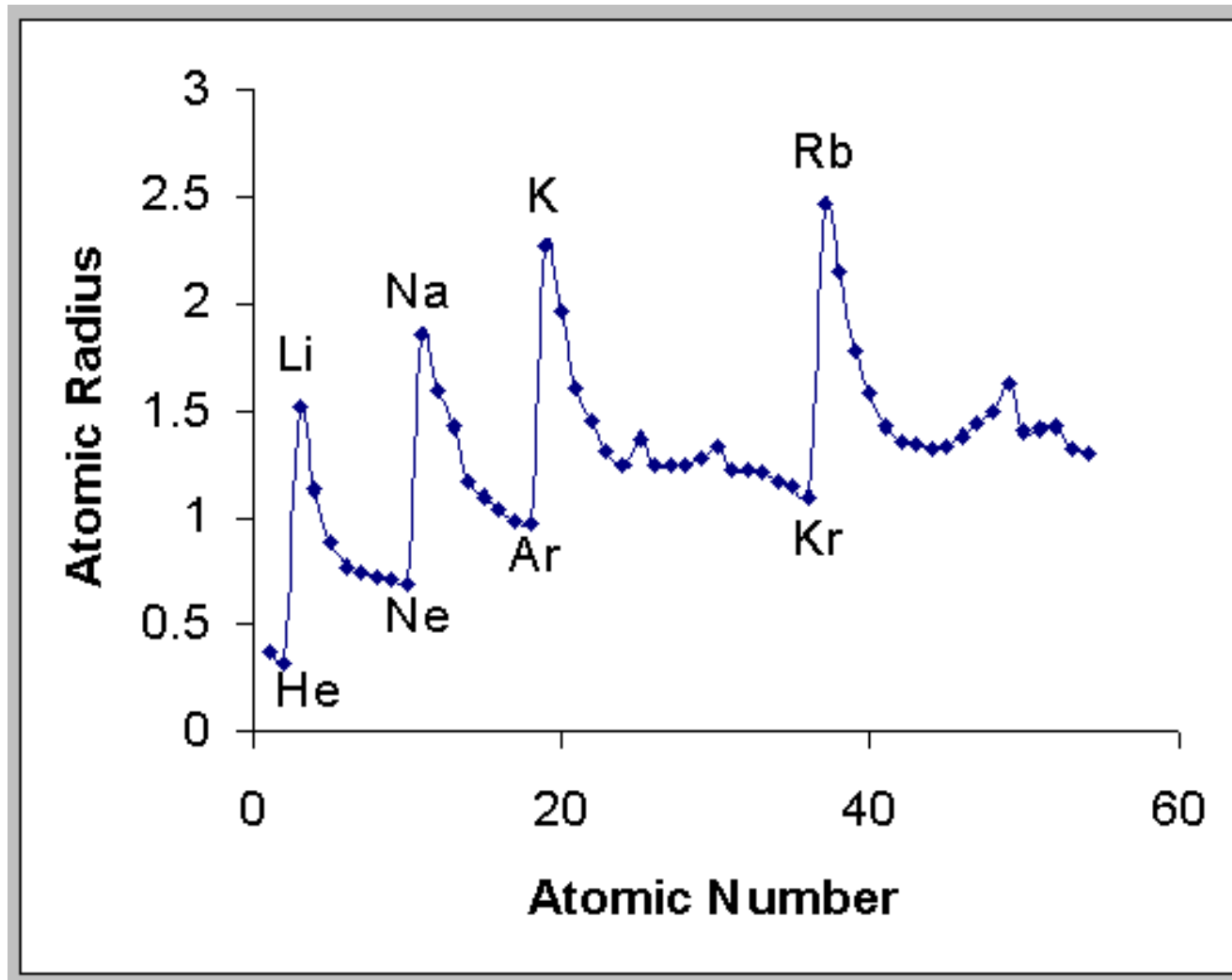
The elements indicated by $[]$ brackets are the noble gases, and these are associated with the complete filling of the p shells, and very stable configuration. They have the highest ionization energies.

Mini-shells, or “half-shells”, indicated by $\{\}$ brackets have very interesting properties. These result in high ionization energies (not as high as the noble gases) indicating that half-shell filling is energetically favored. (This is a result of the spin-orbit interaction, and the preference of electrons to isolate themselves from their fellow identical fermions.)



... Shell structure

More experimental evidence of atomic shell structure is seen in measurements of the atomic radii.



There is quite a difference between the noble gases and the alkali metals!

The best conductors ...



You would be tempted to think that the alkali metals, with their very large radii, would make the best conductors. You'd be wrong!

The best electrical conductors are:

X	structure	electrical resistivity [$n\Omega \cdot m$]
Ag	$[\text{Kr}]5s^14d^{10}$	15.87
Cu	$[\text{Ar}]4s^13d^{10}$	16.78
Au	$[\text{Xe}]6s^15d^{10}4f^{14}$	22.14
Al	$[\text{Ne}]3s^23p^1$	26.50

... The best conductors ...

Al gets its conductivity (the inverse of resistivity) from the loosely-bonded l -shell electron that is promoted to the conduction band in the metal's metallic-crystalline form.

The best conductors are all special cases, and violations of the Madelung rules. The lower d or f -shell, which would normally have 9 or 13 electrons, scavenges an electron to close its shell, taking it from the highest s -shell, that would be normally filled according to Madelung's prescription, leaving one loosely bounded, distant electron to participate on the conduction. [Recall, $r_n = a_0 n^2 / Z$.]

These are the highest-profile Madelung variations. The complete tables of violations is given on the next page.

The periodic table follows on the next page.

Madelung rule violations

Electron shells filled in violation of Madelung's rule^[20] (red)

Period 4			Period 5			Period 6			Period 7		
Element	Z	Electron Configuration	Element	Z	Electron Configuration	Element	Z	Electron Configuration	Element	Z	Electron Configuration
						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
Scandium	21	[Ar] 4s ² 3d ¹	Yttrium	39	[Kr] 5s ² 4d ¹	Lutetium	71	[Xe] 6s ² 4f ¹⁴ 5d ¹	Lawrencium	103	[Rn] 7s ² 5f ¹⁴ 7p ¹
Titanium	22	[Ar] 4s ² 3d ²	Zirconium	40	[Kr] 5s ² 4d ²	Hafnium	72	[Xe] 6s ² 4f ¹⁴ 5d ²	Rutherfordium	104	[Rn] 7s ² 5f ¹⁴ 6d ²
Vanadium	23	[Ar] 4s ² 3d ³	Niobium	41	[Kr] 5s ¹ 4d ⁴	Tantalum	73	[Xe] 6s ² 4f ¹⁴ 5d ³			
Chromium	24	[Ar] 4s ¹ 3d ⁵	Molybdenum	42	[Kr] 5s ¹ 4d ⁵	Tungsten	74	[Xe] 6s ² 4f ¹⁴ 5d ⁴			
Manganese	25	[Ar] 4s ² 3d ⁵	Technetium	43	[Kr] 5s ² 4d ⁵	Rhenium	75	[Xe] 6s ² 4f ¹⁴ 5d ⁵			
Iron	26	[Ar] 4s ² 3d ⁶	Ruthenium	44	[Kr] 5s ¹ 4d ⁷	Osmium	76	[Xe] 6s ² 4f ¹⁴ 5d ⁶			
Cobalt	27	[Ar] 4s ² 3d ⁷	Rhodium	45	[Kr] 5s ¹ 4d ⁸	Iridium	77	[Xe] 6s ² 4f ¹⁴ 5d ⁷			
Nickel	28	[Ar] 4s ² 3d ⁸ or [Ar] 4s ¹ 3d ⁹ (disputed) ^[21]	Palladium	46	[Kr] 4d ¹⁰	Platinum	78	[Xe] 6s ¹ 4f ¹⁴ 5d ⁹			
Copper	29	[Ar] 4s ¹ 3d ¹⁰	Silver	47	[Kr] 5s ¹ 4d ¹⁰	Gold	79	[Xe] 6s ¹ 4f ¹⁴ 5d ¹⁰			
Zinc	30	[Ar] 4s ² 3d ¹⁰	Cadmium	48	[Kr] 5s ² 4d ¹⁰	Mercury	80	[Xe] 6s ² 4f ¹⁴ 5d ¹⁰			

The electron-shell configuration of elements beyond [rutherfordium](#) has not yet been empirically verified, but they are expected to follow Madelung's rule without exceptions until [element 120](#).^[22]

The Periodic Table

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	*	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	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
		*	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	
		**	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	
	Metal Alkali metal Alkaline earth metal Lanthanide Actinide Transition metal Post-transition metal Metalloid Nonmetal Polyatomic nonmetal Diatomic nonmetal Noble gas Unknown chemical properties																	

Transition rates revisited ...

Electromagnetic transitions of excited states are dominated by the $\Delta l = \pm 1$ rule.

The full story will have to await NERS 312, but we will attempt to shed some light on this statement.

Mathematically, the dominant method for producing a γ decay is via the $\vec{x}$ transition, that we have explored in 1D quantum mechanics already. The $\vec{x}$ transition is also called the “dipole” transition.

How does this arise?

The photon wave function has the form:

$$u_\gamma(\vec{x}) = N_\gamma e^{i\vec{k}\cdot\vec{x}}, \quad (8.10)$$

representing a plane wave in the $\hat{k}$ direction.

... Transition rates revisited ...

The transition rate (probability of transition per unit time) between starting level “ i ”, and ending level “ f ” for a hydrogenic atom is:

$$\lambda \propto |\mathcal{M}_{fi}|^2, \quad (8.11)$$

$$\mathcal{M}_{fi} = \langle (nlm_l m_s)_f | e^{i\vec{k} \cdot \vec{x}} | (nlm_l m_s)_i \rangle. \quad (8.12)$$

$\mathcal{M}_{fi}$ is called “the matrix element” or the “transition matrix element”.

In atomic transitions γ decay, as well as in nuclear γ disintegration, the wavelength of the photons that are emitted are well in excess of the atomic, or nuclear size. This allows us to simplify (8.12):

$$\mathcal{M}_{fi} = \langle (nlm_l m_s)_f | \left(1 + i\vec{k} \cdot \vec{x} \right) | (nlm_l m_s)_i \rangle + \mathcal{O}[(\vec{k} \cdot \vec{x})^2]. \quad (8.13)$$

The first term in the expansion, $\langle (nlm_l m_s)_f | (1) | (nlm_l m_s)_i \rangle$, vanishes by orthogonality. Transitions do not occur within a single level, as there is no energy difference to drive the interaction.

Ignoring the $\mathcal{O}[(\vec{k} \cdot \vec{x})^2]$ using the wavelength argument above, we have:

$$\mathcal{M}_{fi} = i\vec{k} \cdot \langle (nlm_l m_s)_f | \vec{x} | (nlm_l m_s)_i \rangle, \quad (8.14)$$

which resembles our 1D discussion in a previous chapter.

... Transition rates revisited ...

Using the explicit forms of the spherical harmonics discussed in the previous chapter, one can show that

$$\begin{aligned}\vec{x} &= r [\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi + \hat{z} \cos \theta] \\ &= r \sqrt{\frac{4\pi}{3}} \left[\frac{Y_{1,1}(\theta, \phi) + Y_{1,-1}(\theta, \phi)}{\sqrt{2}} \hat{x} + \frac{Y_{1,1}(\theta, \phi) - Y_{1,-1}(\theta, \phi)}{\sqrt{2}} \hat{y} + Y_{1,0}(\theta, \phi) \hat{z} \right] .\end{aligned}\quad (8.15)$$

Without loss of generality, assume that that $\vec{k}$ is directed along the positive z -axis. Then, using the fact that the transition does not flip the intrinsic spin of the wavefunction,

$$\mathcal{M}_{fi} = ik \sqrt{\frac{4\pi}{3}} \langle n_f l_f | r | n_i l_i \rangle \int_{4\pi} d\Omega Y_{l_f, m_{l,f}}^*(\theta, \phi) Y_{1,0}(\theta, \phi) Y_{l_i, m_{l,i}}(\theta, \phi) . \quad (8.16)$$

It can be shown that the angular integral is only non-zero when the m_l 's are the same, and when $l_f = l_i \pm 1$. $\therefore$

$$\mathcal{M}_{fi} = Ck \langle n_f(l_i \pm 1) | r | n_i l_i \rangle , \quad (8.17)$$

where C is some constant that can be established by doing the angular integral.

... Transition rates revisited

This explains the $\Delta l = \pm 1$ rule. There is still a radial integral to do, which in most cases, will be non-zero.

Of course, there are other transitions that happen between larger differences in l . These are much more improbable, but they do exist. We shall explore them in NERS 312.

Coupling spins ...

When $\vec{l}$ and $\vec{s}$ become strongly coupled $\mathcal{L}$ is no longer a constant of the motion. It is quantized, but not constant.

In atomic physics they are weakly coupled, and spin-orbit and spin-spin interactions may be treated using perturbation theory, where $\vec{l}$ and $\vec{s}$ are treated as if they are constant, and the resulting error is negligible.

In nuclear physics, this coupling is very strong and perturbative approaches are not practical.

However, for both cases, total angular momentum is conserved, and is a constant of the motion. Therefore, to proceed further, we have to introduce the method of spin coupling. It resembles classical mechanics, but the methods are completely different.

The total angular momentum for each particle in quantum mechanics, called $\vec{j}$ is given as a sum of its orbital and intrinsic spins, namely:

$$\vec{j} = \vec{l} + \vec{s}. \quad (8.18)$$

However, in quantum mechanics, these are operators with the following properties:

... Coupling spins ...

$$\begin{aligned}\langle J^2 \rangle &= \hbar^2 j(j+1) && \text{total angular momentum operator, and its eigenvalue} \\ \langle J_z \rangle &= \hbar m_j && \text{magnetic angular momentum operator, and its eigenvalue}\end{aligned}\quad (8.19)$$

j may be integral, or half integral.

The rules for the formulation and discretization of j and m_j are:

The procedure is completely general for coupling any quantum spins, l , s , or j . Starting with a given l and s :

1. Form the set of j 's that are coupled to, from a given l and s .
 - (a) The minimum possible j is $|l - s|$
 - (b) The maximum possible j is $|l + s|$
 - (c) The set of independent j_i 's is $j_i = \{j_{\max}, j_{\max} - 1 \cdots j_{\min}\}$
 - (d) The number of independent j 's is $n_j = j_{\max} - j_{\min} + 1$
2. For each j_i , form the m_j , using integral jumps from $-j$ to j .

Some examples are in order!

... Coupling spins ...

Example 1

Question: *An electron is in a p state in a Hydrogen atom. What are the possible j values?*

Answer: Following the steps on the previous page explicitly:

1. Form the set of j 's that are coupled to, from the given $l = 1$ and $s = \frac{1}{2}$ for an electron.
 - (a) The minimum possible j is $|1 - \frac{1}{2}| = \frac{1}{2}$
 - (b) The maximum possible j is $|1 + \frac{1}{2}| = \frac{3}{2}$
 - (c) The set of independent j_i 's is $j_i = \{j_{\max}, j_{\max} - 1 \cdots j_{\min}\} = \{\frac{3}{2}, \frac{1}{2}\}$
 - (d) The number of independent j 's is $n_j = \frac{3}{2} - \frac{1}{2} + 1 = 2$, as expected
2. For $j_i = \frac{3}{2}$, form the $m_j = (-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$
For $j_i = \frac{1}{2}$, form the $m_j = (-\frac{1}{2}, \frac{1}{2})$

Note from the statement of the problem, there are $3m_l$ states and $2m_s$ states. So, in combination, there are 6 independent states, having quantum numbers:
 $|l, m_l, m_s\rangle = |1, 1, \frac{1}{2}\rangle, |1, 0, \frac{1}{2}\rangle, |1, -1, \frac{1}{2}\rangle, |1, 1, -\frac{1}{2}\rangle, |1, 0, -\frac{1}{2}\rangle, |1, -1, -\frac{1}{2}\rangle$

Thus we expect 6 independent $|j, m_j\rangle$ states, and they have been found to be:
 $|j, m_j\rangle = |\frac{3}{2}, -\frac{3}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, \frac{3}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle$

... Coupling spins ...

Example 2

Question: $l = 2$, $s = \frac{1}{2}$. What are the possible j values?

Answer: Following the steps on the previous page explicitly:

1. Form the set of j 's that are coupled to, from the given $2 = 1$ and $s = \frac{1}{2}$.

Note that this implies that there are 10 independent states.

(a) The minimum possible j is $|2 - \frac{1}{2}| = \frac{3}{2}$

(b) The maximum possible j is $|2 + \frac{1}{2}| = \frac{5}{2}$

(c) The set of independent j_i 's is $j_i = \{j_{\max}, j_{\max} - 1 \cdots j_{\min}\} = \{\frac{5}{2}, \frac{3}{2}\}$

(d) The number of independent j 's is $n_j = \frac{5}{2} - \frac{3}{2} + 1 = 2$, as expected

2. For $j_i = \frac{5}{2}$, form the $m_j = (-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2})$

$j_i = \frac{3}{2}$, form the $m_j = (-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$

Note from the statement of the problem, there are $5m_l$ states and $2m_s$ states.

So, in combination, there are 10 independent states, having quantum numbers:

$$|l, m_l, m_s\rangle = |2, 2, \pm\frac{1}{2}\rangle, |2, 1, \pm\frac{1}{2}\rangle, |2, 0, \pm\frac{1}{2}\rangle, |2, -1, \pm\frac{1}{2}\rangle, |2, -2, \pm\frac{1}{2}\rangle,$$

Thus we expect 10 independent $|j, m_j\rangle$ states, and they have been found to be:

$$|j, m_j\rangle = |\frac{5}{2}, -\frac{5}{2}\rangle, |\frac{5}{2}, -\frac{3}{2}\rangle, |\frac{5}{2}, -\frac{1}{2}\rangle, |\frac{5}{2}, \frac{1}{2}\rangle, |\frac{5}{2}, \frac{3}{2}\rangle, |\frac{5}{2}, \frac{5}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, \frac{3}{2}\rangle$$

... Coupling spins ...

Coupling 2 orbital angular momenta

Let the total angular momentum, $\vec{L}$, arising from two single-particle angular momenta, $\vec{l}_1 + \vec{l}_2$ be:

$$\vec{L} = \vec{l}_1 + \vec{l}_2 \quad (8.20)$$

$$L^2 = \hbar^2 L(L + 1) \quad (8.21)$$

$$L_z = \hbar m_L \quad (8.22)$$

$$L_{\min} = |l_1 - l_2| \quad (8.23)$$

$$L_{\max} = |l_1 + l_2| \quad (8.24)$$

$$L_{\min} \leq L_i \leq L_{\max} \quad [\text{integral jumps}] \quad (8.25)$$

$$n_L = L_{\max} - L_{\min} + 1 \quad [\text{number of independent } L\text{'s}] \quad (8.26)$$

$$L_i = L_{\min}, L_{\min} + 1 \cdots L_{\max} \quad [\text{the independent } L\text{'s}] \quad (8.27)$$

$$m_L = 0, \pm 1, \pm 2, \cdots \pm L_i \quad [\text{integral jumps}] \quad (8.28)$$

... Coupling spins ...

Example 3:

Question: $l_1 = 3, l_2 = 2. L = ?$

Answer:

Note that $l_1 = 3, l_2 = 2 \Rightarrow D = 7 \times 5 = 35. D = \text{degeneracy}.$

$$1 \leq L \leq 5$$

L	m_L	D
1	$0, \pm 1$	3
2	$0, \pm 1, \pm 2$	5
3	$0, \pm 1, \pm 2, \pm 3$	7
4	$0, \pm 1, \pm 2, \pm 3, \pm 4$	9
5	$0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5$	11
		$\sum D = 35$

... Coupling spins ...

Coupling 2 intrinsic $\frac{1}{2}$ spins

Let the total spin angular momentum, $\vec{S}$, arising from two single-particle $\frac{1}{2}$ spins, $\vec{s}_1 + \vec{s}_2$, be:

$$\vec{S} = \vec{s}_1 + \vec{s}_2 \quad (8.29)$$

$$S^2 = \hbar^2 S(S+1) = \frac{3}{4}\hbar^2 \quad (8.30)$$

$$S_z = \hbar m_S \quad (8.31)$$

$$S_{\min} = |s_1 - s_2| = 0 \quad (8.32)$$

$$S_{\max} = |s_1 + s_2| = 1 \quad (8.33)$$

$$S_i = 0, 1 \quad [\text{the independent } S\text{'s}] \quad (8.34)$$

Example 4:

$$\frac{1}{2} + \frac{1}{2} = ?$$

$$S = 0; \quad m_S = 0$$

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

... Coupling spins ...

Coupling many orbital and spin angular momenta

$$\vec{L} = \sum_{i=1}^N \vec{l}_i \quad (8.35)$$

$$\vec{S} = \sum_{i=1}^N \vec{s}_i \quad (8.36)$$

$$\vec{J} = \vec{L} + \vec{S} = \sum_{i=1}^N (\vec{l}_i + \vec{s}_i) = \sum_{i=1}^N \vec{j}_i \quad [\text{many alternative forms}] \quad (8.37)$$

Do the couplings two at a time.

Example 5:

$$\frac{\vec{1}}{2} + \frac{\vec{1}}{2} + \frac{\vec{1}}{2} = ?$$

... Coupling spins ...

Coupling many orbital and spin angular momenta

Rewrite as:

$$\begin{aligned}\frac{\vec{1}}{2} + \frac{\vec{1}}{2} + \frac{\vec{1}}{2} &= \left\{ \left(\frac{\vec{1}}{2} + \frac{\vec{1}}{2} \right) + \frac{\vec{1}}{2} \right\} & D = 2 \times 2 \times 2 = 8 \\ &= \left\{ \{ \vec{1}, \vec{0} \} + \frac{\vec{1}}{2} \right\} & \text{from Example 4} \\ &= \left\{ \left(\vec{1} + \frac{\vec{1}}{2} \right), \left(\vec{0} + \frac{\vec{1}}{2} \right) \right\} & \text{redistributing} \\ &= \left\{ \left(\vec{1} + \frac{\vec{1}}{2} \right), \frac{\vec{1}}{2} \right\} & \text{since } \vec{0} + \frac{\vec{1}}{2} = \frac{\vec{1}}{2} \\ &= \left\{ \left\{ \frac{\vec{3}}{2}, \frac{\vec{1}}{2} \right\}, \frac{\vec{1}}{2} \right\} & \text{from Example 1} \\ &= \left\{ \frac{\vec{3}}{2}, \frac{\vec{1}}{2}, \frac{\vec{1}}{2} \right\} & \text{collapsing, note there are two } \frac{\vec{1}}{2} \text{ states}\end{aligned}$$

S	m_S	D
$\frac{1}{2}$	$\pm \frac{1}{2}$	2
$\frac{1}{2}$	$\pm \frac{1}{2}$	2 (degenerate with state above)
$\frac{3}{2}$	$\pm \frac{3}{2}, \pm \frac{1}{2}$	4

$$\sum D = 8, \text{ as expected}$$

Coupling momenta in many-electron atoms, Hund's rules ...

Hund's rules:

1. Find the maximum M_S consistent with the Pauli Exclusion Principle. Set $S = M_S$.
2. For that M_S , find the maximum M_L . Set $L = M_L$.

Note:

Closed shells are indicated by $\uparrow\downarrow$'s.

This implies that $L = 0$, and $S = 0$ for closed shells.

... Coupling momenta in many-electron atoms, Hund's rules ...

Examples:

He: $\vec{S} = \frac{1}{2} + \frac{1}{2}$
 $1s \uparrow\downarrow$ (the two $1s$ spins cancel each other)
 $S = 0; \max(M_S) = 0$

[He]: $L = 0, S = 0$

Li: $[\text{He}]s^1$ treat as single particle

$2s \uparrow$

$S = \frac{1}{2}; \max(M_S) = \frac{1}{2}$

Li : $L = 0, S = \frac{1}{2}$

Be: $[\text{He}]s^2$

$2s \uparrow\downarrow$ (the two $1s$ spins cancel each other)

$\max(M_S) = 0$ (Pauli) $\Rightarrow S = 0$

Be : $L = 0, S = 0$

... Coupling momenta in many-electron atoms, Hund's rules ...

B: $[\text{He}]s^22p^1$ treat as a single particle

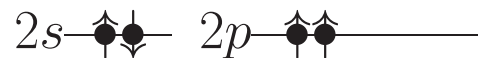


$$\max(M_S) = \frac{1}{2} \Rightarrow S = \frac{1}{2}$$

$$\max(M_L) = 1 \Rightarrow L = 1$$

$$\text{B : } L = 1, S = \frac{1}{2}$$

C: $[\text{He}]s^22p^2$ treat as two particles outside the closed $2s^2$ shell



$$\max(M_S) = 1 \Rightarrow S = 1$$

$$\max(M_L) = 1 \Rightarrow L = 1$$

$$\text{C : } L = 1, S = 1$$

N: $[\text{He}]s^22p^3$ treat as three particles outside the closed $2s^2$ shell



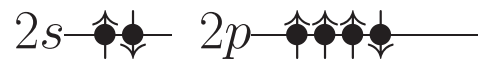
$$\max(M_S) = \frac{3}{2} \Rightarrow S = \frac{3}{2}$$

$$\max(M_L) = 0 \Rightarrow L = 0$$

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

... Coupling momenta in many-electron atoms, Hund's rules ...

O: $[\text{He}]s^22p^4$ treat as four particles outside the closed $2s^2$ shell

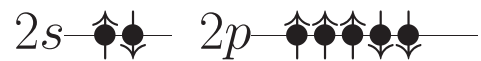


$$\max(M_S) = 1 \Rightarrow S = 1$$

$$\max(M_L) = 1 \Rightarrow L = 1$$

O: $L = 1, S = 1$

F: $[\text{He}]s^22p^5$ treat as five particles outside the closed $2s^2$ shell

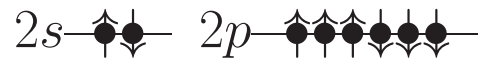


$$\max(M_S) = \frac{1}{2} \Rightarrow S = \frac{1}{2}$$

$$\max(M_L) = 1 \Rightarrow L = 1$$

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

[Ne]: $L = 0, S = 0$



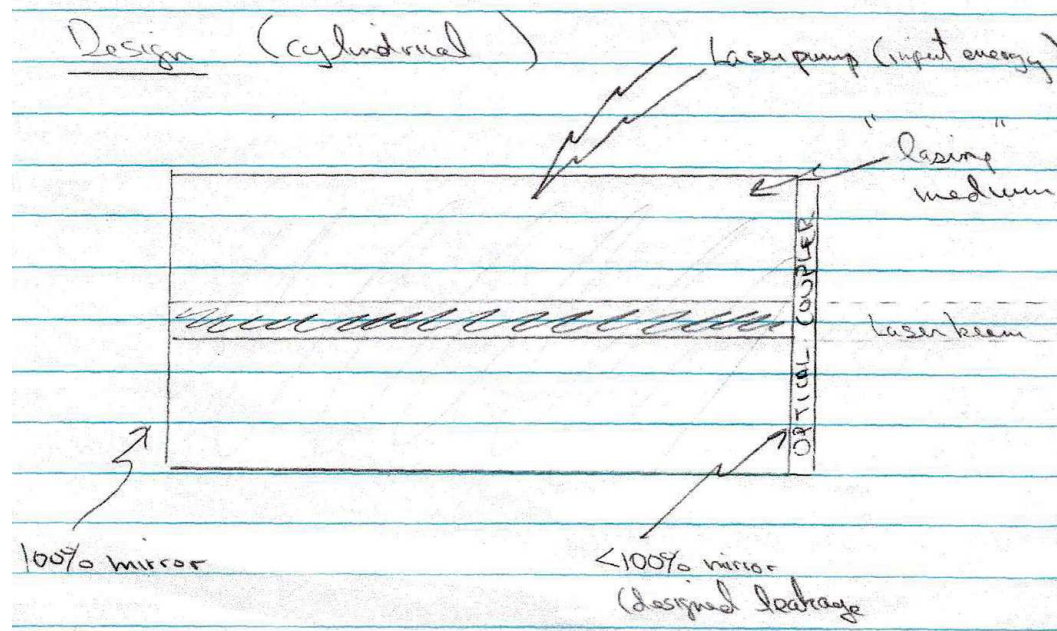
⋮

Lasers ...

Light Amplification by Stimulated Emission of Radiation

Lasers provide a source of mono-energetic, coherent light.

monoenergetic	one energy
coherent	monodirectional peaks and valleys of all single photon wavefunctions are aligned

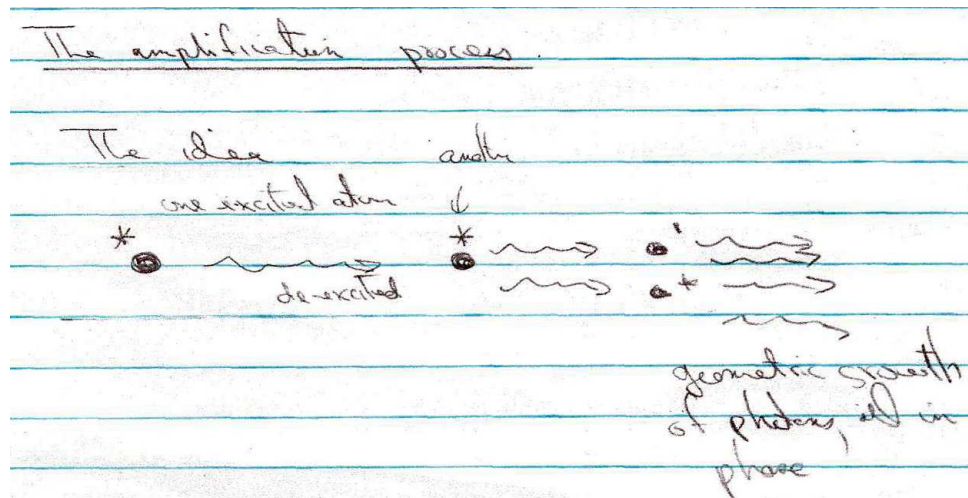


... Lasers ...

Components of a laser

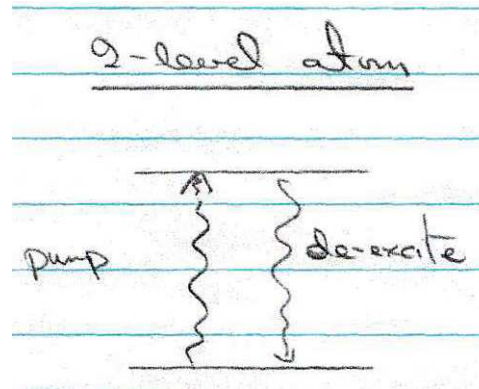
laser pump	electrical discharge current, incoherent light source
“lasing” medium	or “amplification” medium (where the quantum-mechanical magic occurs) [more on this later]
100% mirror	reflects all the light, can also be used to focus
< 100% mirror	designed to reflect almost all of the light, but allows some controlled leakage into the optical coupler
optical coupler	lens

The amplification process



... Lasers ...

A single atom, two-level lasing medium ...

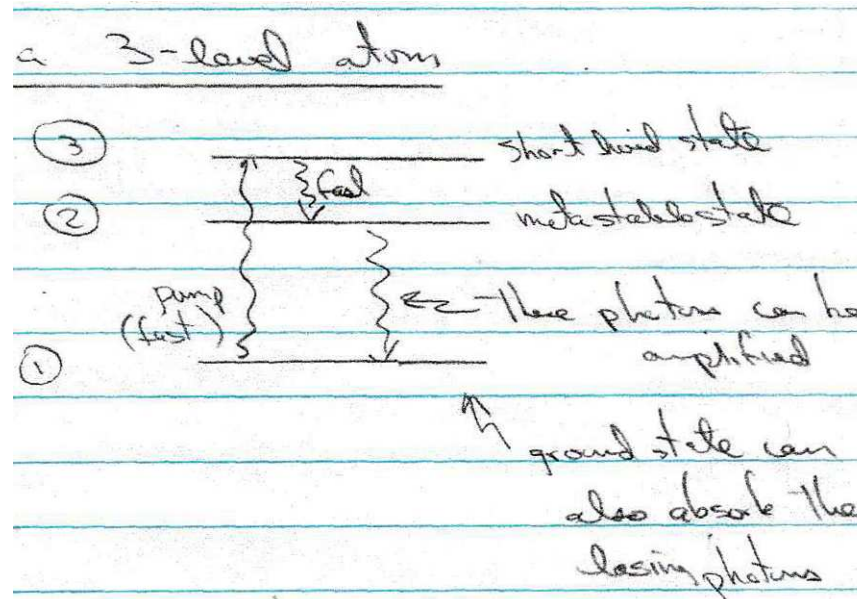


... does not “lase”, because the pump and the de-excitation are in direct competition with each other $\Rightarrow$ no amplification

- The medium absorbs the lasing photons.
- Pumping depletes the ground state.

... Lasers ...

A single atom, three-level lasing medium ...

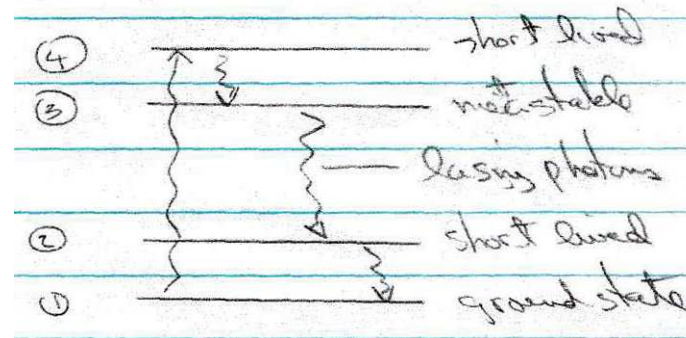


does “lase”, but it is not ideal

- There is “population inversion”, *i.e.* more atoms at energy-level 2, than at 1, but de-excitation depopulates level 2, and populates level 1, reducing the inversion.
- The ground state absorbs the lasing photons

... Lasers ...

A single atom, four-level lasing medium ...



is ideal

- There is a large population inversion
- The ground state does not absorb the lasing photons

On the next page is a description of a very efficient two atom, four level lasing medium.

... Lasers ...

A two-atom, four-level efficient lasing medium ...

