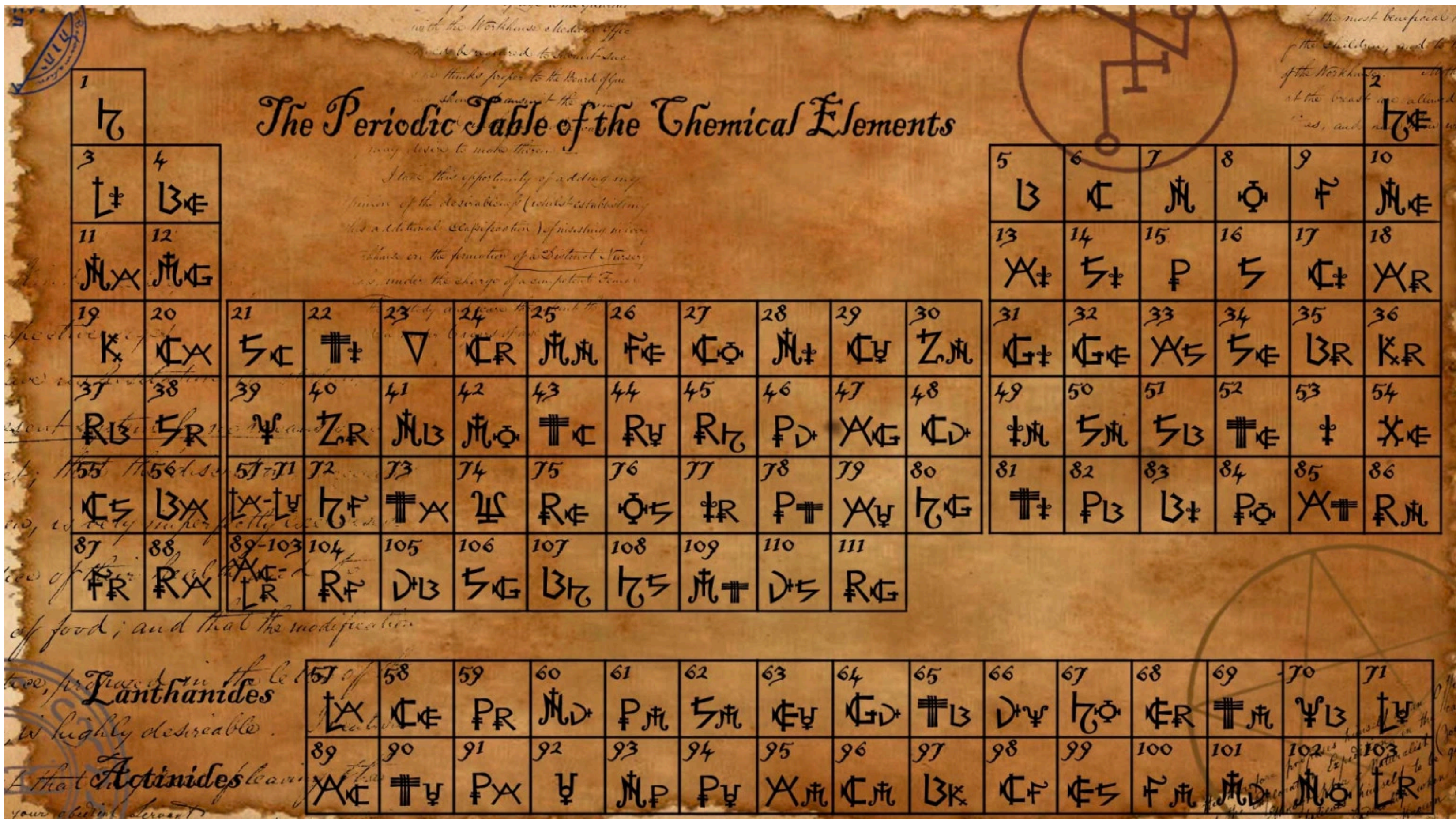
Atomic Physics

Chapter 5 Structure of the Periodic system

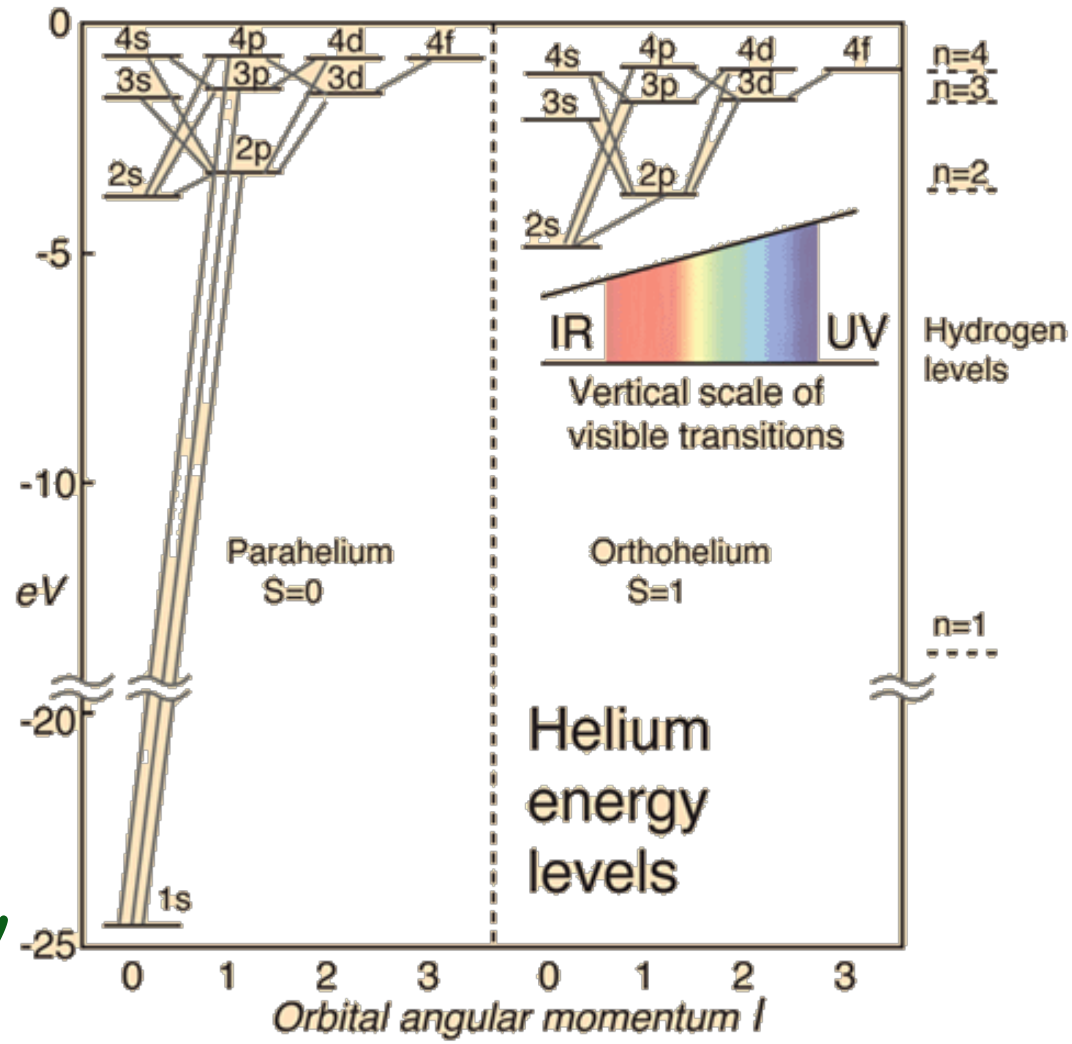


The spectra of helium

1. Two sets:
   parahelium
   orthohelium

2. Orthohelium has fine structure

3. The energy difference between the ground state and the lowest excited state in helium is relatively large.



The coupling of electrons

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The electron configuration is the distribution of electrons of an atom in atomic orbitals.

$$nl,\ nln'l',\ nln'l'n''l'',\ \ldots$$

For the two-electron atom, we label the electrons 1 and 2. The total angular momentum J is the vector sum of the four angular momenta:

$$\vec{J} = \vec{l}_1 + \vec{l}_2 + \vec{s}_1 + \vec{s}_2$$

There are two schemes, called LS coupling and jj coupling, for combining the four angular momenta to form J. The decision of which scheme to use depends on relative strengths of the various interactions. We shall see that jj coupling predominates for heavier elements.

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The LS coupling scheme, also called Russell-Saunders coupling, is used for most atoms when the coupling between the orbital angular momenta of electrons is strong.

A total orbital angular momentum and spin,

$$\vec{L} = \vec{L}_1 + \vec{L}_2$$

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

Then L and S combine to form the total angular momentum:

$$\vec{J} = \vec{L} + \vec{S}$$

The coupling of two electrons

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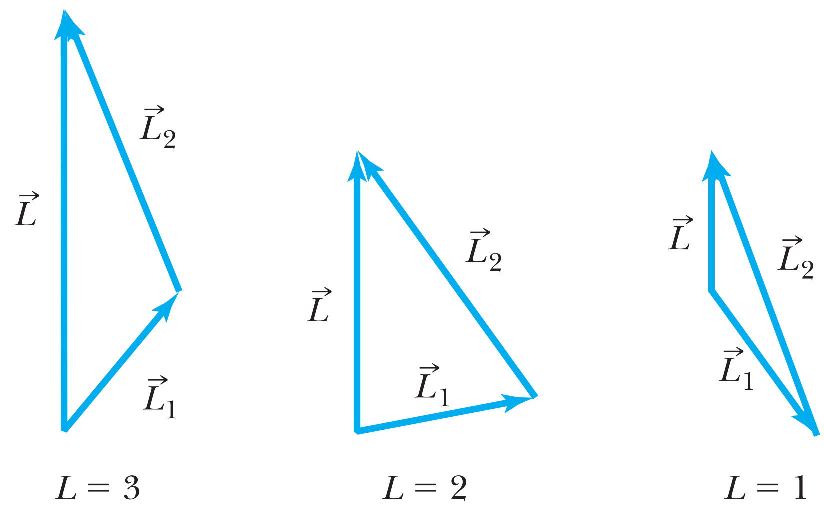
The coupling of two angular momenta

$$L_1 = \sqrt{l_1(l_1+1)}\hbar$$

$$L_2 = \sqrt{l_2(l_2+1)}\hbar$$

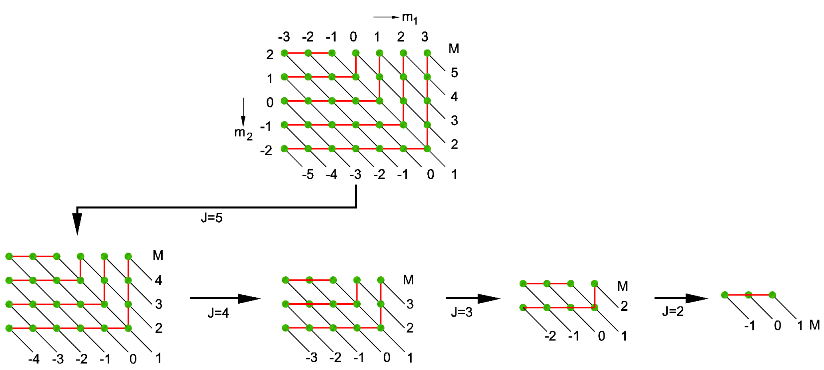
$$L = \sqrt{l(l+1)}\hbar$$



where,

$$l = |l_1 - l_2|, |l_1 - l_2| + 1, |l_1 - l_2| + 2, \ldots, |l_1 + l_2|$$

$$m = m_1 + m_2$$



The coupling of two electrons

For the case of two electrons in a single subshell, the total spin angular momentum quantum number may be S=0 or 1.

For a given value of L, there are 2S+1 values of J, because J goes from L-S to L+S (for L>S).

The value of 2S+1 is called the multiplicity of the state.

The notation nl discussed before for a single-electron atom becomes

$$n^{2S+1}L_J$$

The letters and numbers used in this notation are called spectroscopic or term symbols.

The coupling of two electrons

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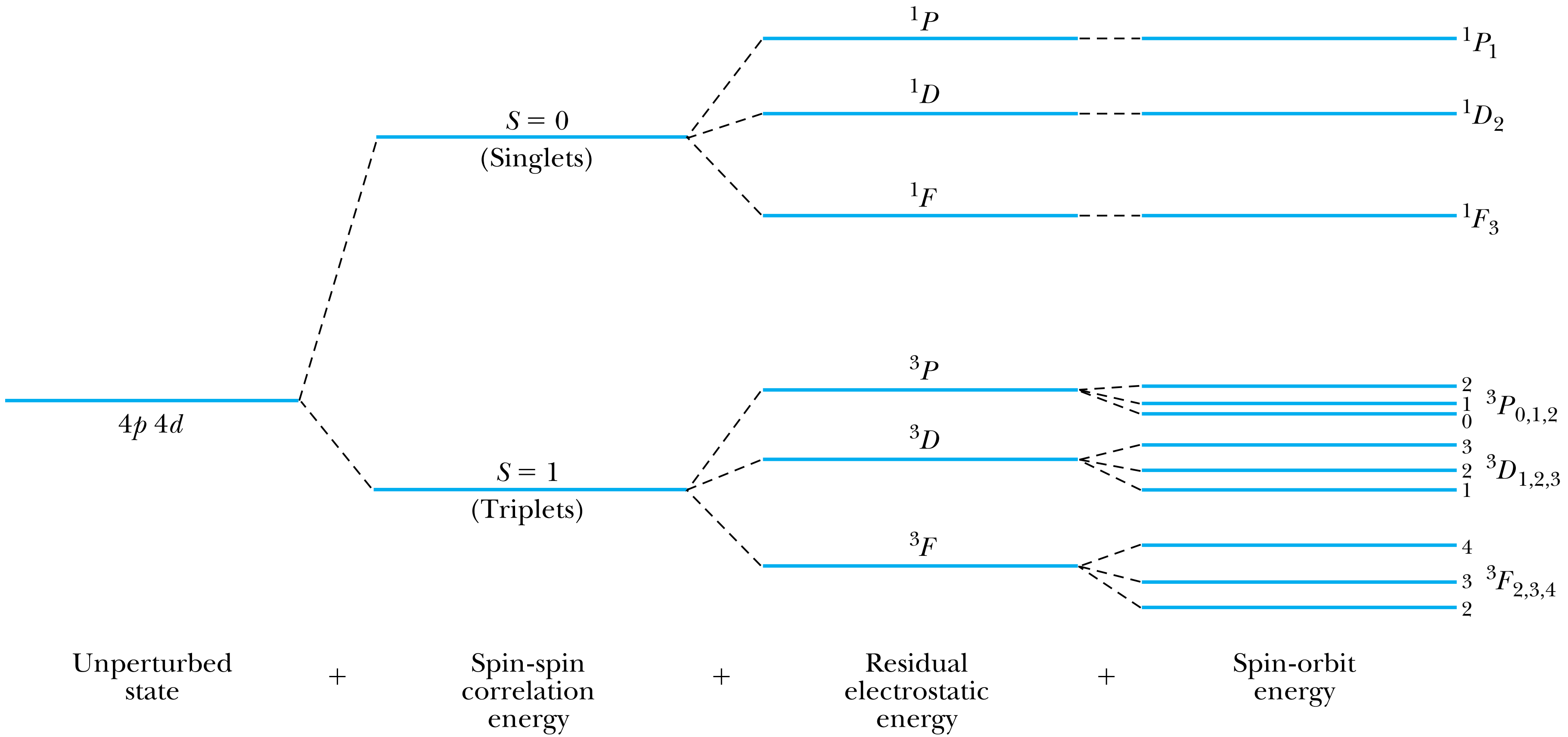
For two electrons we have singlet states (S=0) and triplet states (S=1), which refer to the multiplicity 2S+1.

Consider two electrons: One is in the 4p and one is in the 4d subshell. For the atomic states shown

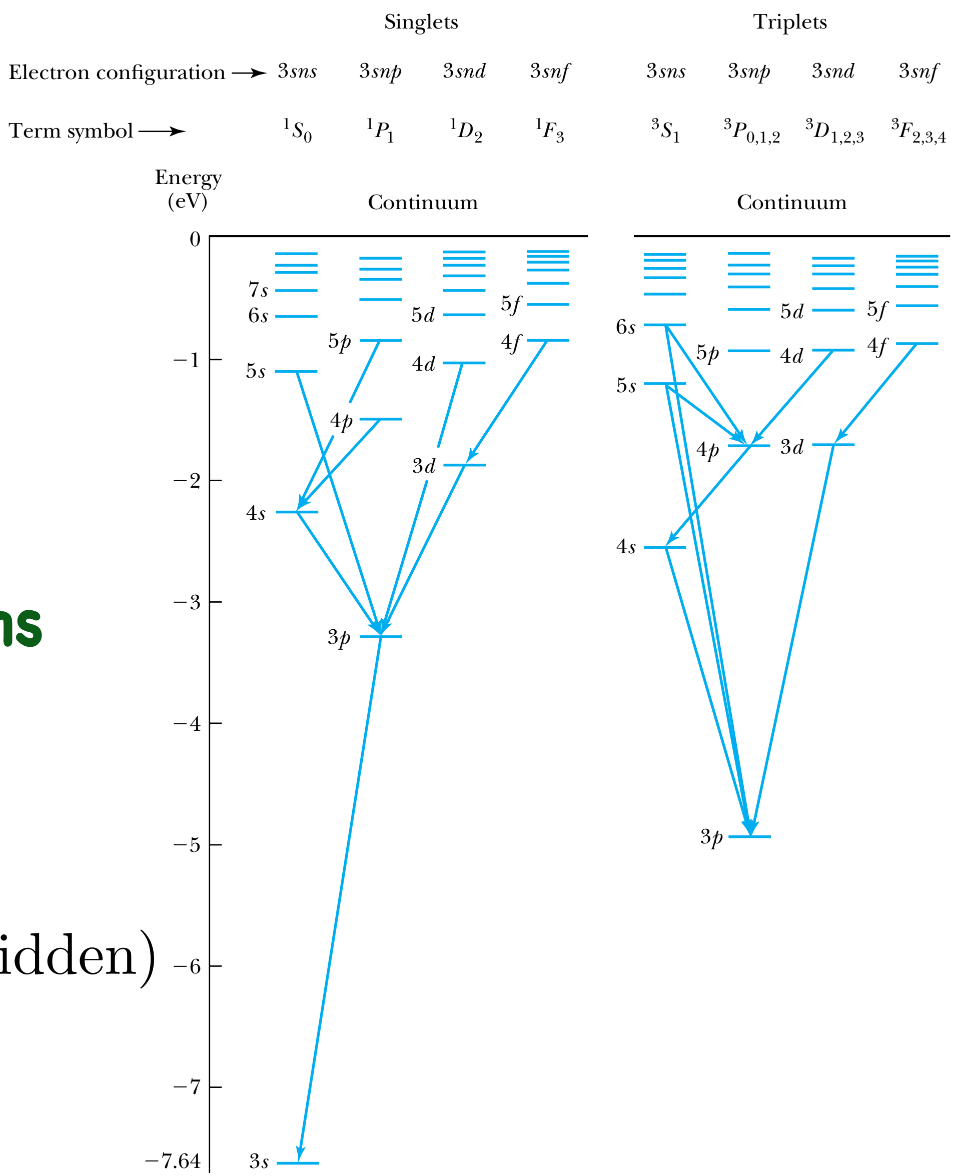
S	L	J	Spectroscopic Symbol
0 (singlet)	1	1	4^1P_1
	2	2	4^1D_2
	3	3	4^1F_3
1 (triplet)	1	2	4^3P_2
		1	4^3P_1
		0	4^3P_0
1 (triplet)	2	3	4^3D_3
		2	4^3D_2
		1	4^3D_1
1 (triplet)	3	4	4^3F_4
		3	4^3F_3
		2	4^3F_2

A schematic diagram showing the relative energies of these states appears



The coupling of two electrons

As an example of the optical spectra obtained from two electron atoms, we consider the energy-level diagram of magnesium.



The choice rules of transitions (for LS coupling scheme) are

$$\Delta L = \pm 1 \qquad \Delta S = 0$$

$$\Delta J = 0, \pm 1 \quad (J = 0 \rightarrow J = 0 \ \ \text{forbidden})$$

The coupling of two electrons

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jj coupling scheme predominates for the heavier elements, where the nuclear charge causes the spin-orbit interactions to be as strong as the forces between the individual spin and the individual orbit angular momentum. The coupling order becomes

$$\vec{J}_1 = \vec{L}_1 + \vec{S}_1$$

$$\vec{J}_2 = \vec{L}_2 + \vec{S}_2$$

and then

$$\vec{J} = \sum_i J_i$$

The choice rules of transitions (for jj coupling scheme) are

$$\Delta j = 0, \pm 1 \qquad \Delta J = 0, \pm 1$$

$$(J = 0 \rightarrow J' = 0 \quad \text{forbidden})$$

The allowed transitions

The allowed transitions for a single-electron atom are

$$\Delta l = \pm 1 \qquad \Delta m_j = 0, \ \pm 1$$

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

The choice rules of transitions (for LS coupling scheme) are

$$\Delta L = \pm 1 \qquad \Delta S = 0$$

$$\Delta J = 0, \pm 1 \quad (J = 0 \to J = 0 \ \ \text{forbidden})$$

The choice rules of transitions for jj coupling are

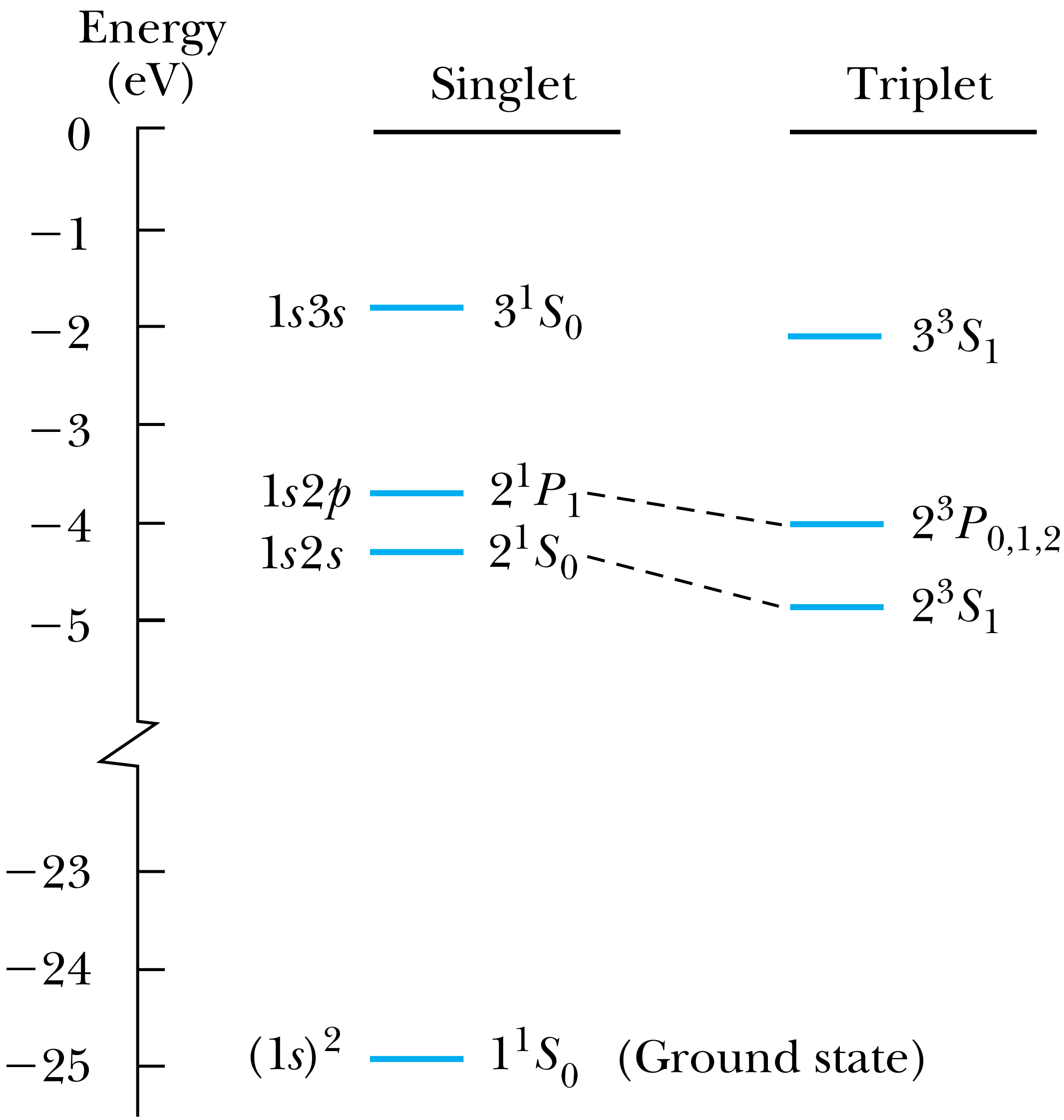
$$\Delta j = 0, \pm 1 \qquad \Delta J = 0, \pm 1$$

$$(J = 0 \to J' = 0 \ \ \text{forbidden})$$

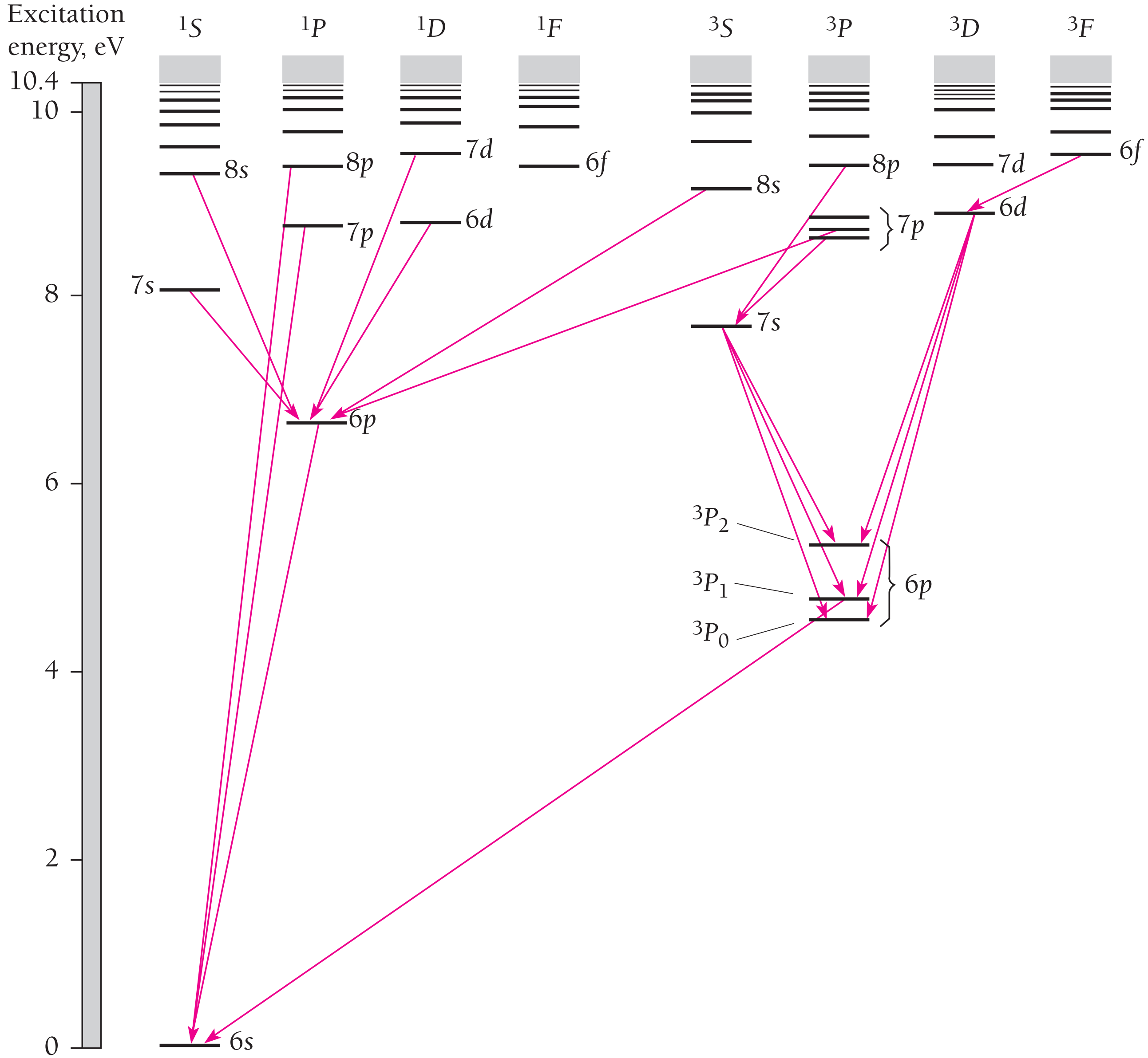
The parity requirement

$$\sum l_i - \sum l_f = \pm 1$$

The spectra of helium



The spectra of Mercy



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Pauli exclusion principle: No two electrons in an atom may have the same set of quantum numbers

$$n,\ l,\ m_l,\ m_s$$

Pauli's exclusion principle applies to all particles of half-integer spin, which are called fermions, and can be generalized to include particles in the nucleus.

The complete wave function of a system of n noninteracting particles can be expressed as the product of the wave functions

$$\psi(1,\ 2,\ 3,\ldots,\ n) = \psi(1)\psi(2)\psi(3)\ldots\psi(n)$$

Pauli exclusion principle

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Exchange symmetry of probability density for 2 states

$$|\psi|^2(1,2) = |\psi|^2(2,1)$$

Symmetric

$$\psi(1,2) = \psi(2,1)$$

Antisymmetric

$$\psi(1,2) = -\psi(2,1)$$

The corresponding wave functions

$$\psi_S = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$$

$$\psi_A = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

Pauli exclusion principle

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There are a number of important distinctions between the behavior of particles in systems whose wave functions are symmetric and that of particles in systems whose wave functions are antisymmetric.

In the antisymmetric case, if we set a=b, we find that

$$\psi_A = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_a(2) - \psi_a(2)\psi_a(1)] = 0$$

Hence the two particles cannot be in the same quantum state. Systems of electrons are described by wave functions that reverse sign upon the exchange of any pair of them.

Pauli exclusion principle

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The results of various experiments show that all particles which have odd half-integral spins have wave functions that are antisymmetric to an exchange of any pair of them.

Particles of odd half-integral spin are often referred to as fermions.

Particles whose spins are 0 or an integer have wave functions that are symmetric to an exchange of any pair of them. Particles of 0 or integral spin are often referred to as bosons

The applications

The ground state of Helium

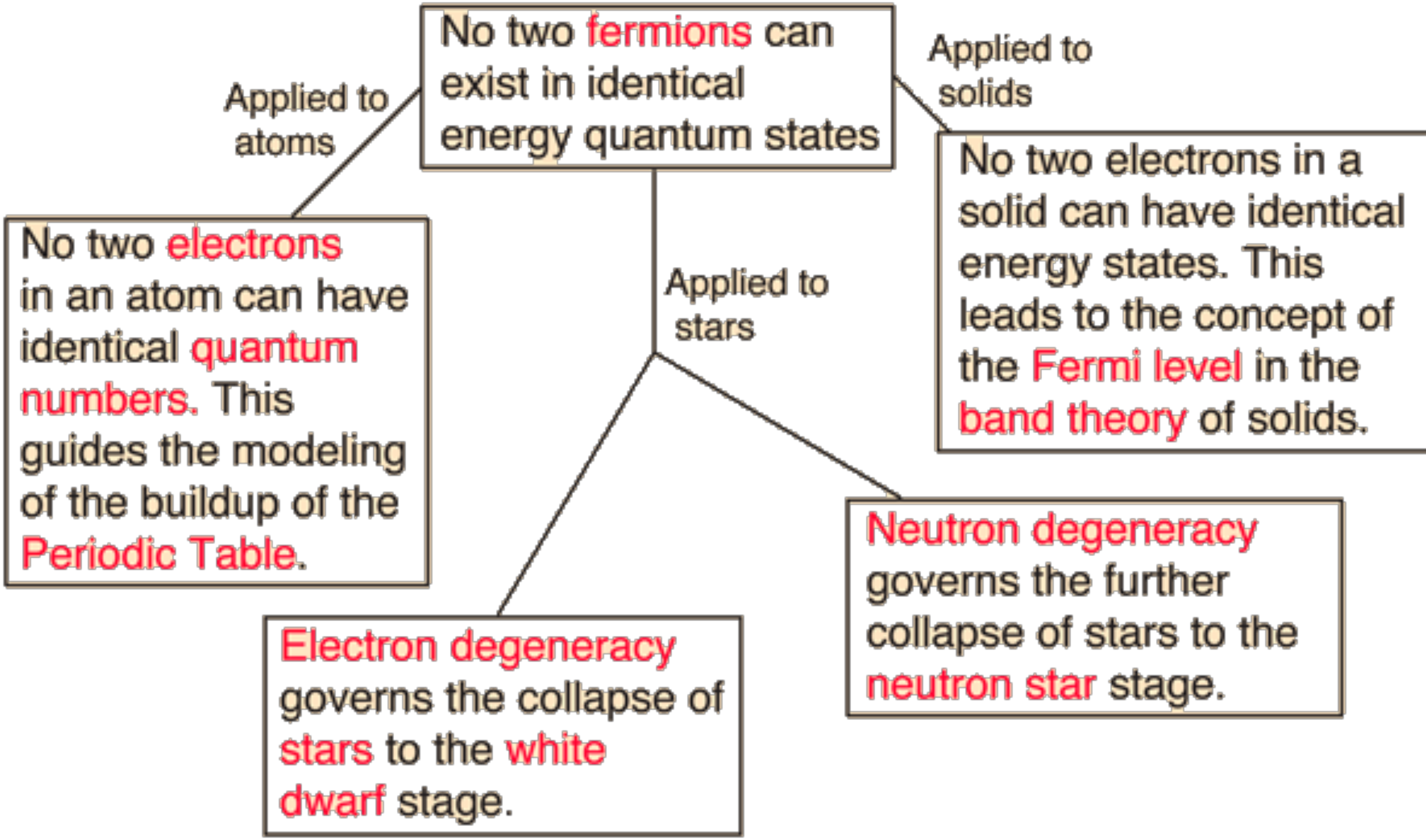
The size of atom

The atom of metal

The independent motion of nucleon

The colors of quarks

The applications



The equivalent electrons

Equivalent electrons: those which belong to same (n,l) sub-shells

The coupling of two equivalent electrons: allowed combinations must of course be consistent with Pauli Exclusion Principle (all quantum numbers cannot be same)

np^2

m												
1	↑↓			↑		↑	↑		↑	↑		↓
0		↑↓		↓	↑		↑	↑		↓	↓	
-1			↑↓		↓	↓		↑	↑		↑	↑
M_L	2	0	-2	1	-1	0	1	0	-1	1	0	-1
M_S	0	0	0	0	0	0	1	1	1	0	0	0
	$^1D_2$					$^1S_0$	$^3P_{2,1,0}$					

Electronic terms for atoms with equivalent electron configurations

Configuration	Electronic terms	Atoms
$p\ p^5$	^2P	B, F
$p^2\ p^4$	$^1S\ ^3P\ ^1D$	C, O, N^+
p^3	$^4S\ ^2P\ ^2D$	N, O^+
p^6	^1S	Ne
$d\ d^9$	^2D	Sc
$d^2\ d^8$	$^1S\ ^3P\ ^1D\ ^3F\ ^1G$	Ti, Ni
$d^3\ d^7$	$^2P\ ^4P\ 2^2D\ ^2F\ ^4F\ ^2G\ ^2H$	V, Co
$d^4\ d^6$	$2^1S\ 2^3P\ 2^1D\ ^3D\ ^5D\ ^1F$ $2^3F\ 2^1G\ ^3G\ ^3H\ ^1I$	Fe
d^5	$^2S\ ^6S\ ^2P\ ^4P\ 3^2D\ ^4D\ 2^2F$ $^4F\ 2^2G\ ^4G\ ^2H\ ^2I$	Mn
d^{10}	^1S	Zn

Evalid terms for subshells of q electrons are the same as for subshells with N-q electrons where N is the closed (full) subshell complement

Periodic Table of Elements

Closed shells | Alkalis | Alkaline earths | Transition elements (groups 3–12) | Halogens | Rare gases

Closed shells	1 (Alkalis)	2 (Alkaline earths)	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17 (Halogens)	18 (Rare gases)
	1 **H** $1s$																	2 **He** $1s^2$
$1s^2$	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2\ 2p^1$	6 **C** $2s^2\ 2p^2$	7 **N** $2s^2\ 2p^3$	8 **O** $2s^2\ 2p^4$	9 **F** $2s^2\ 2p^5$	10 **Ne** $2s^2\ 2p^6$
$2s^22p^6$	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2\ 3p^1$	14 **Si** $3s^2\ 3p^2$	15 **P** $3s^2\ 3p^3$	16 **S** $3s^2\ 3p^4$	17 **Cl** $3s^2\ 3p^5$	18 **Ar** $3s^2\ 3p^6$
$3s^23p^6$	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^1\ 4s^2$	22 **Ti** $3d^2\ 4s^2$	23 **V** $3d^3\ 4s^2$	24 **Cr** $3d^5\ 4s^1$	25 **Mn** $3d^5\ 4s^2$	26 **Fe** $3d^6\ 4s^2$	27 **Co** $3d^7\ 4s^2$	28 **Ni** $3d^8\ 4s^2$	29 **Cu** $3d^{10}\ 4s^1$	30 **Zn** $3d^{10}\ 4s^2$	31 **Ga** $3d^{10}\ 4s^2\ 4p^1$	32 **Ge** $3d^{10}\ 4s^2\ 4p^2$	33 **As** $3d^{10}\ 4s^2\ 4p^3$	34 **Se** $3d^{10}\ 4s^2\ 4p^4$	35 **Br** $3d^{10}\ 4s^2\ 4p^5$	36 **Kr** $3d^{10}\ 4s^2\ 4p^6$
$3d^{10}4s^24p^6$	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^1\ 5s^2$	40 **Zr** $4d^2\ 5s^2$	41 **Nb** $4d^4\ 5s^1$	42 **Mo** $4d^5\ 5s^1$	43 **Tc** $4d^6\ 5s^1$	44 **Ru** $4d^7\ 5s^1$	45 **Rh** $4d^8\ 5s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}\ 5s^1$	48 **Cd** $4d^{10}\ 5s^2$	49 **In** $4d^{10}\ 5s^2\ 5p^1$	50 **Sn** $4d^{10}\ 5s^2\ 5p^2$	51 **Sb** $4d^{10}\ 5s^2\ 5p^3$	52 **Te** $4d^{10}\ 5s^2\ 5p^4$	53 **I** $4d^{10}\ 5s^2\ 5p^5$	54 **Xe** $4d^{10}\ 5s^2\ 5p^6$
$4d^{10}5s^25p^6$	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $5d^1\ 6s^2$	72 **Hf** $4f^{14}\ 5d^2\ 6s^2$	73 **Ta** $4f^{14}\ 5d^3\ 6s^2$	74 **W** $4f^{14}\ 5d^4\ 6s^2$	75 **Re** $4f^{14}\ 5d^5\ 6s^2$	76 **Os** $4f^{14}\ 5d^6\ 6s^2$	77 **Ir** $4f^{14}\ 5d^9$	78 **Pt** $4f^{14}\ 5d^9\ 6s^1$	79 **Au** $4f^{14}\ 5d^{10}\ 6s^1$	80 **Hg** $4f^{14}\ 5d^{10}\ 6s^2$	81 **Tl** $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$	82 **Pb** $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$	83 **Bi** $4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$	84 **Po** $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$	85 **At** $4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$	86 **Rn** $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$
$4f^{14}5d^{10}6s^26p^6$	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $6d^1\ 7s^2$	104 **Rf** $5f^{14}\ 6d^2\ 7s^2$	105 **Db** $5f^{14}\ 6d^3\ 7s^2$	106 **Sg** $5f^{14}\ 6d^4\ 7s^2$	107 **Bh** $5f^{14}\ 6d^5\ 7s^2$	108 **Hs** $5f^{14}\ 6d^6\ 7s^2$	109 **Mt** $5f^{14}\ 6d^7\ 7s^2$	110 **Ds** $5f^{14}\ 6d^9\ 7s^1$	111 **Rg** $5f^{14}\ 6d^{10}\ 7s^1$	112 **Cn** $5f^{14}\ 6d^{10}\ 7s^2$						

Lanthanides	58 **Ce** $4f^2\ 6s^2$	59 **Pr** $4f^3\ 6s^2$	60 **Nd** $4f^4\ 6s^2$	61 **Pm** $4f^5\ 6s^2$	62 **Sm** $4f^6\ 6s^2$	63 **Eu** $4f^7\ 6s^2$	64 **Gd** $4f^7\ 6s^2\ 5d^1$	65 **Tb** $4f^9\ 6s^2$	66 **Dy** $4f^{10}\ 6s^2$	67 **Ho** $4f^{11}\ 6s^2$	68 **Er** $4f^{12}\ 6s^2$	69 **Tm** $4f^{13}\ 6s^2$	70 **Yb** $4f^{14}\ 6s^2$	71 **Lu** $4f^{14}\ 5d^1\ 6s^2$
Actinides	90 **Th** $6d^2\ 7s^2$	91 **Pa** $5f^2\ 6d^1\ 7s^2$	92 **U** $5f^3\ 6d^1\ 7s^2$	93 **Np** $5f^4\ 6d^1\ 7s^2$	94 **Pu** $5f^6\ 7s^2$	95 **Am** $5f^7\ 7s^2$	96 **Cm** $5f^7\ 6d^1\ 7s^2$	97 **Bk** $5f^8\ 6d^1\ 7s^2$	98 **Cf** $5f^{10}\ 7s^2$	99 **Es** $5f^{11}\ 7s^2$	100 **Fm** $5f^{12}\ 7s^2$	101 **Md** $5f^{13}\ 7s^2$	102 **No** $5f^{14}\ 7s^2$	103 **Lr** $5f^{14}\ 6d^1\ 7s^2$

The ionization energies of the element

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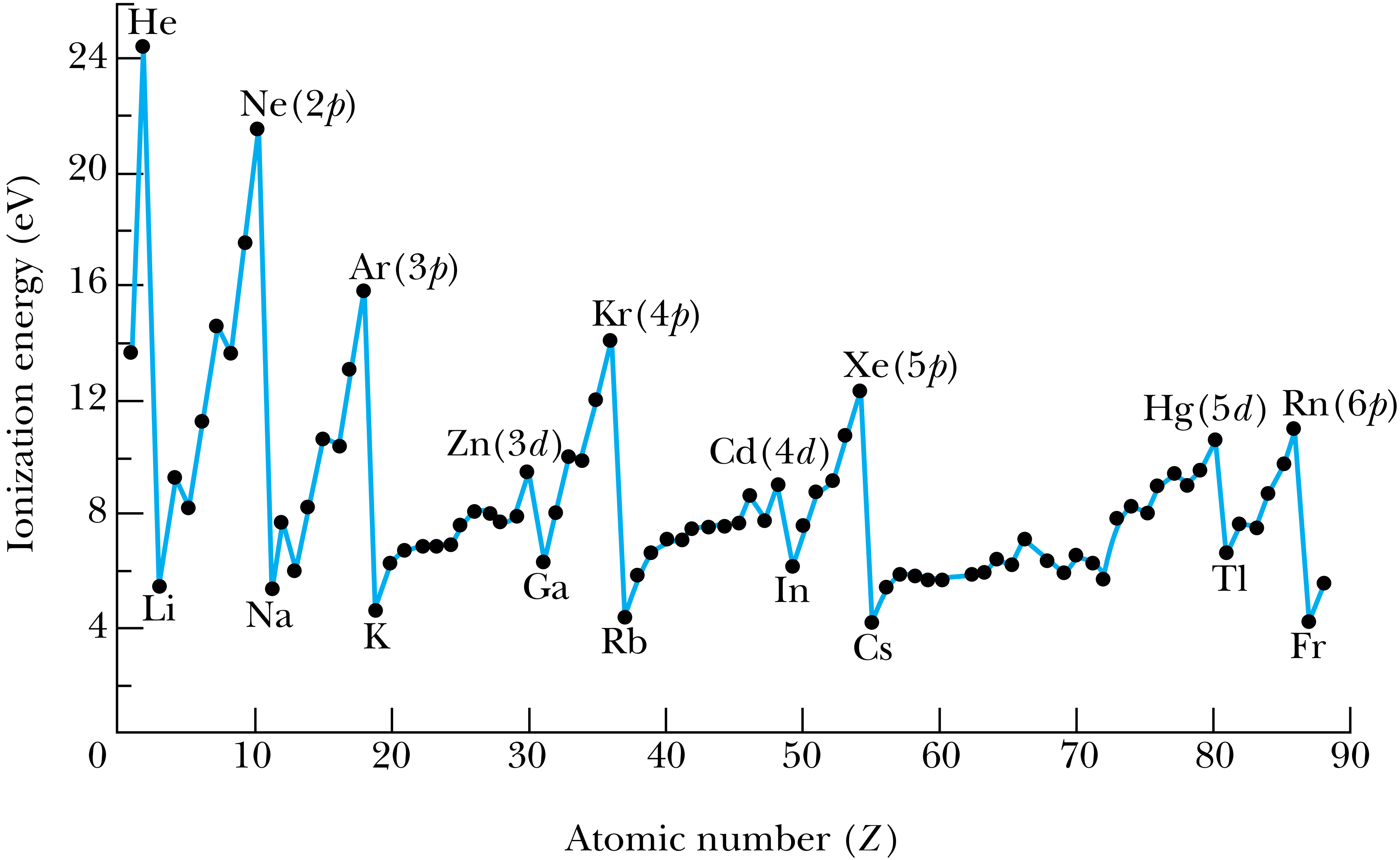
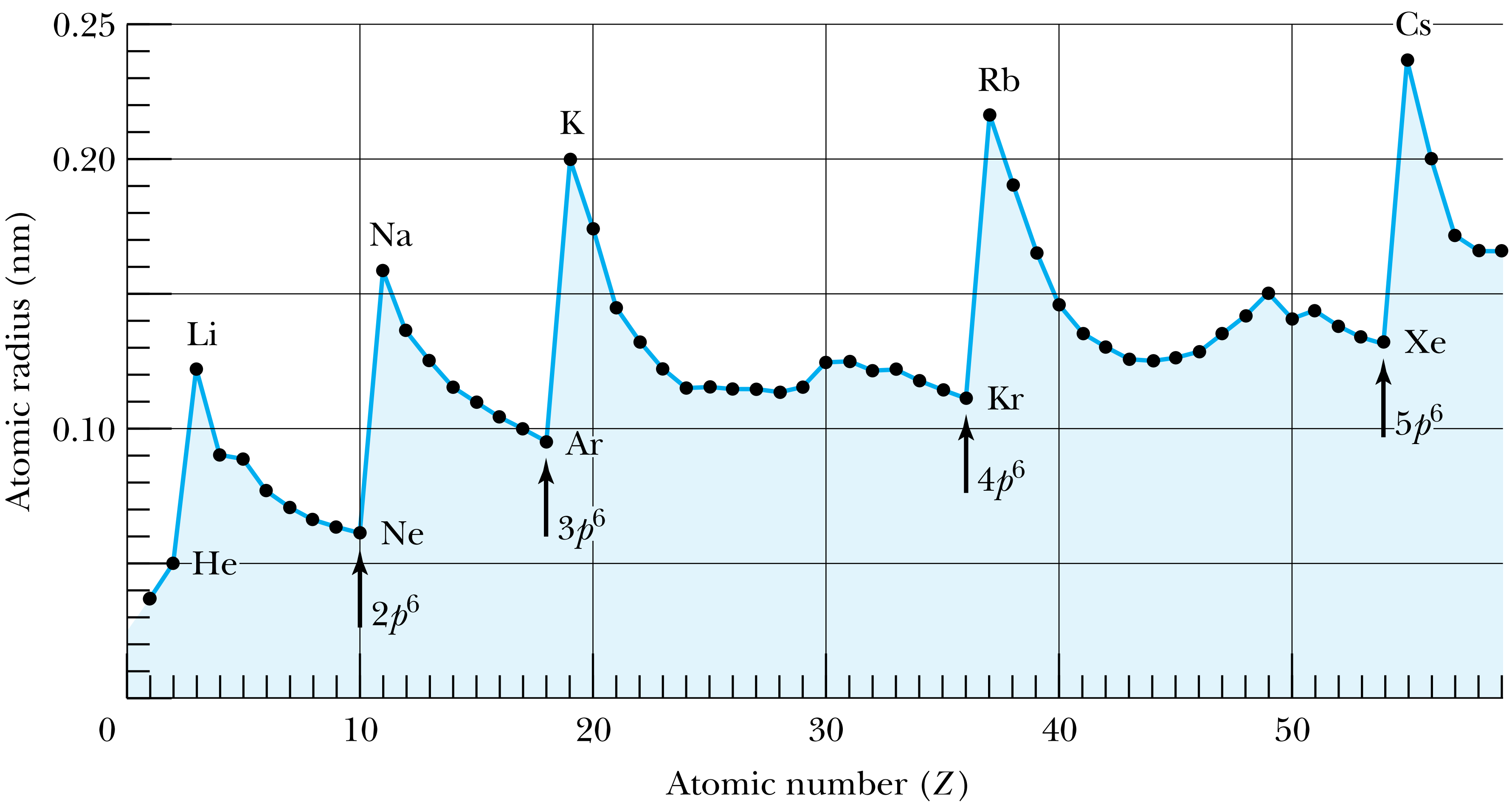


Atomic radii



The shell and subshell

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The atomic electron structure leading to the observed ordering of the periodic table can be understood by the application of two rules:

1. The electrons in an atom tend to occupy the lowest energy levels available to them.
2. Only one electron can be in a state with a given (complete) set of quantum numbers (Pauli exclusion principle).

The shell and subshell

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Electrons that have the same principal quantum number n usually (though not always) average roughly the same distance from the nucleus. It is conventional to speak of such electrons as occupying the same atomic shell.

Electrons that share a certain value of l in a shell are said to occupy the same subshell.

	$m_l = 0$	$m_l = -1$	$m_l = +1$	$m_l = -2$	$m_l = +2$	
$l = 0$:	$\downarrow\uparrow$					$\uparrow m_s = +\frac{1}{2}$
$l = 1$:	$\downarrow\uparrow$	$\downarrow\uparrow$	$\downarrow\uparrow$			$\downarrow m_s = -\frac{1}{2}$
$l = 2$:	$\downarrow\uparrow$	$\downarrow\uparrow$	$\downarrow\uparrow$	$\downarrow\uparrow$	$\downarrow\uparrow$	

The occupancy of the various subshells in an atom is usually expressed with the help of electron configurations for the various quantum states of the hydrogen atom. For example, the electron configuration of sodium is written

$$1s^2 2s^2 2p^6 3s^1$$

which means that the 1s (n=1, l=0)
and 2s (n=2, l=0) subshells contain two electrons each,
the 2p (n=2, l=1) subshell contains six electrons,
and the 3s (n=3, l=0) subshell contains one electron.

Shell and subshell capacities

How many electrons may be in each subshell in order not to violate the Pauli exclusion principle?

	Total
For each m_ℓ: two values of m_s	2
For each ℓ: $(2\ell + 1)$ values of m_ℓ	$2(2\ell + 1)$

The maximum number of electrons a shell can hold is the sum of the electrons in its filled subshells. This number is

$$N_{\max} = \sum_{l=0}^{l=n-1} 2(2l+1)$$

$$= 2n^2$$

Thus a closed K shell holds 2 electrons, a closed L shell holds 8 electrons, a closed M shell holds 18 electrons, and so on.

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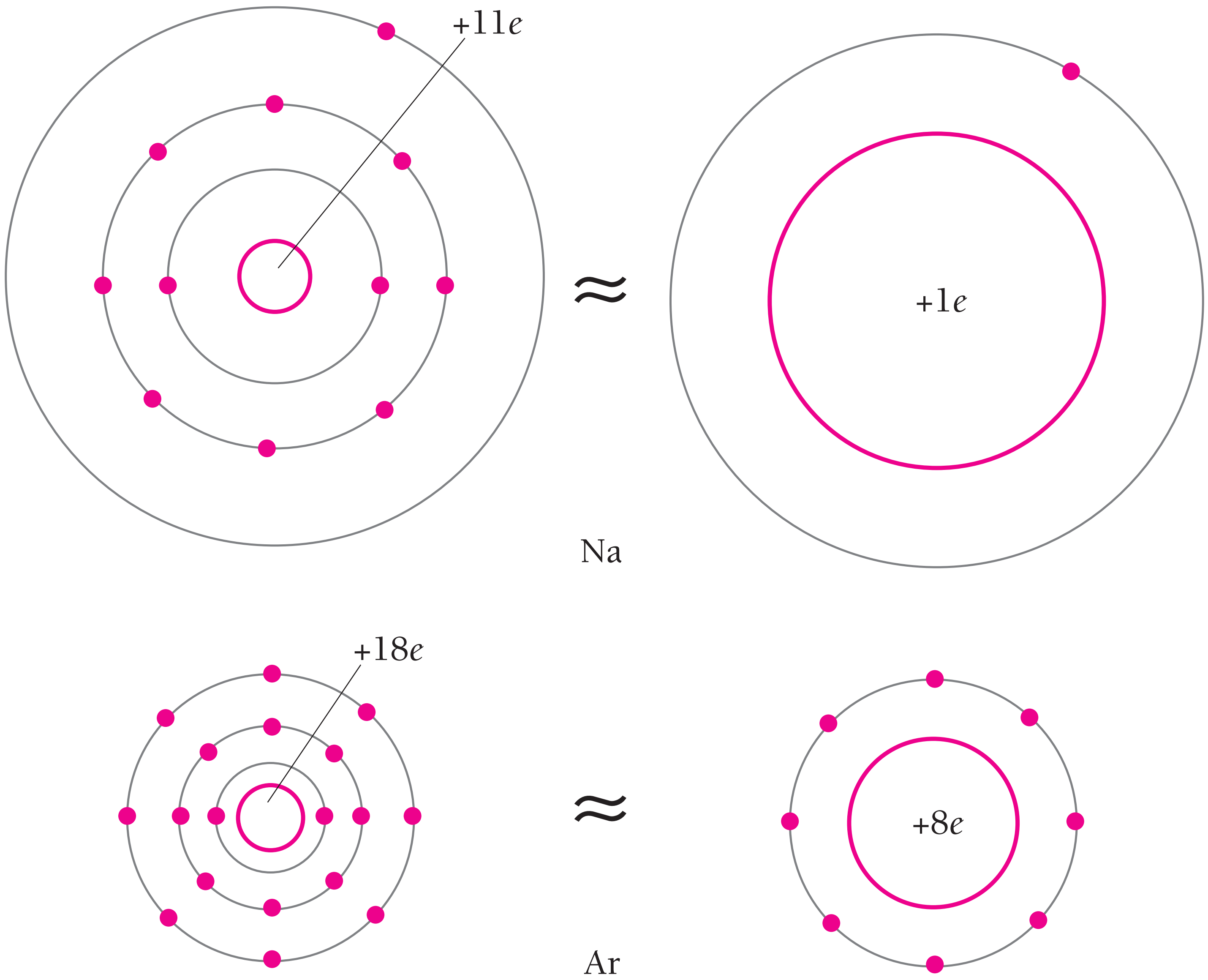
An atomic shell or subshell that contains its full quota of electrons is said to be closed. A closed s subshell (l=0) holds two electrons, a closed p subshell (l=1) six electrons, a closed d subshell (l=2) ten electrons, and so on.

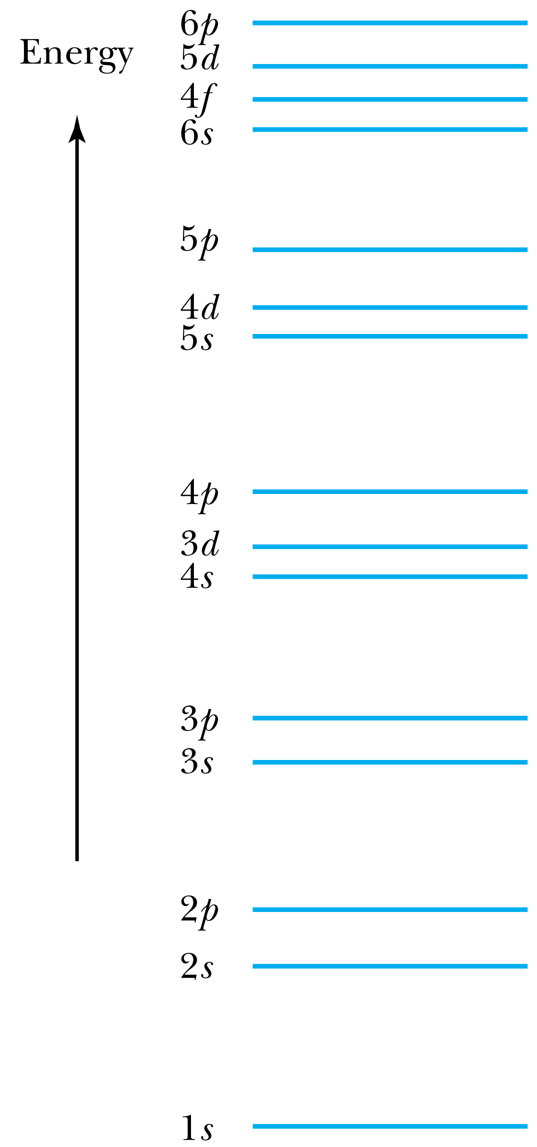
The total orbital and spin angular momenta of the electrons in a closed subshell are zero, and their effective charge distributions are perfectly symmetrical.

The electrons in a closed shell are all very tightly bound, since the positive nuclear charge is large relative to the negative charge of the inner shielding electrons

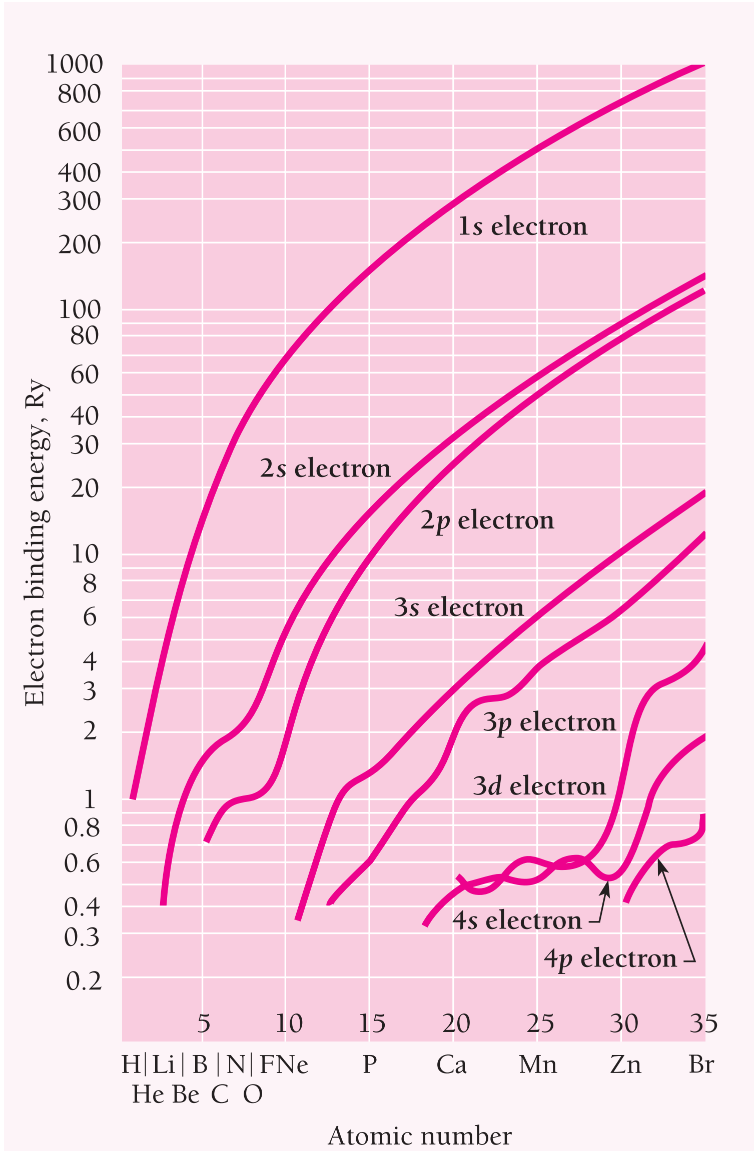

+11e
+1e
Na
+18e
+8e
Ar

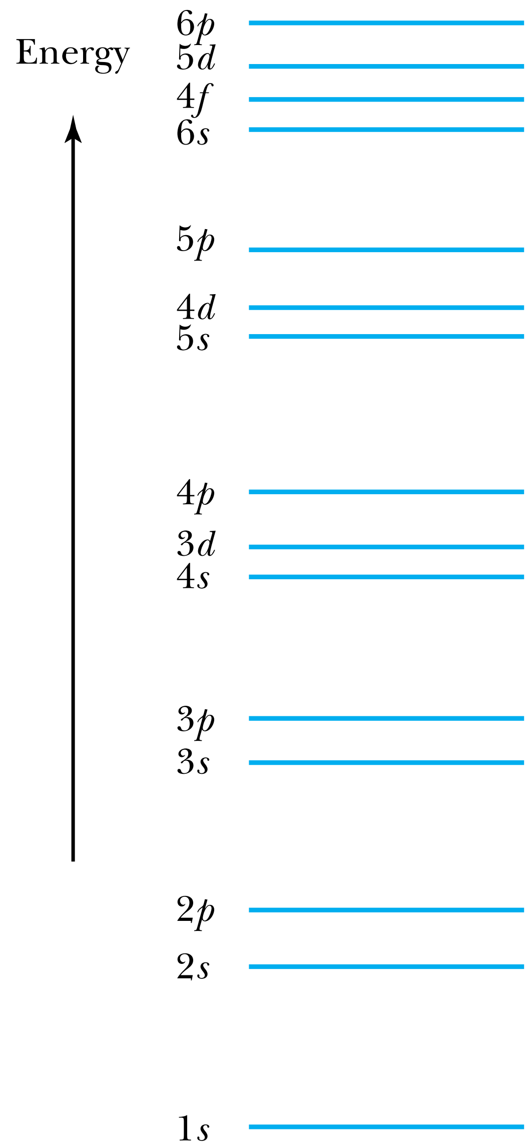
Shell and subshell capacities

n	ℓ	Subshell	Subshell Capacity	Total Electrons in All Subshells
1	0	1*s*	2	2
2	0	2*s*	2	4
2	1	2*p*	6	10
3	0	3*s*	2	12
3	1	3*p*	6	18
4	0	4*s*	2	20
3	2	3*d*	10	30
4	1	4*p*	6	36
5	0	5*s*	2	38
4	2	4*d*	10	48
5	1	5*p*	6	54
6	0	6*s*	2	56
4	3	4*f*	14	70
5	2	5*d*	10	80
6	1	6*p*	6	86
7	0	7*s*	2	88
5	3	5*f*	14	102
6	2	6*d*	10	112

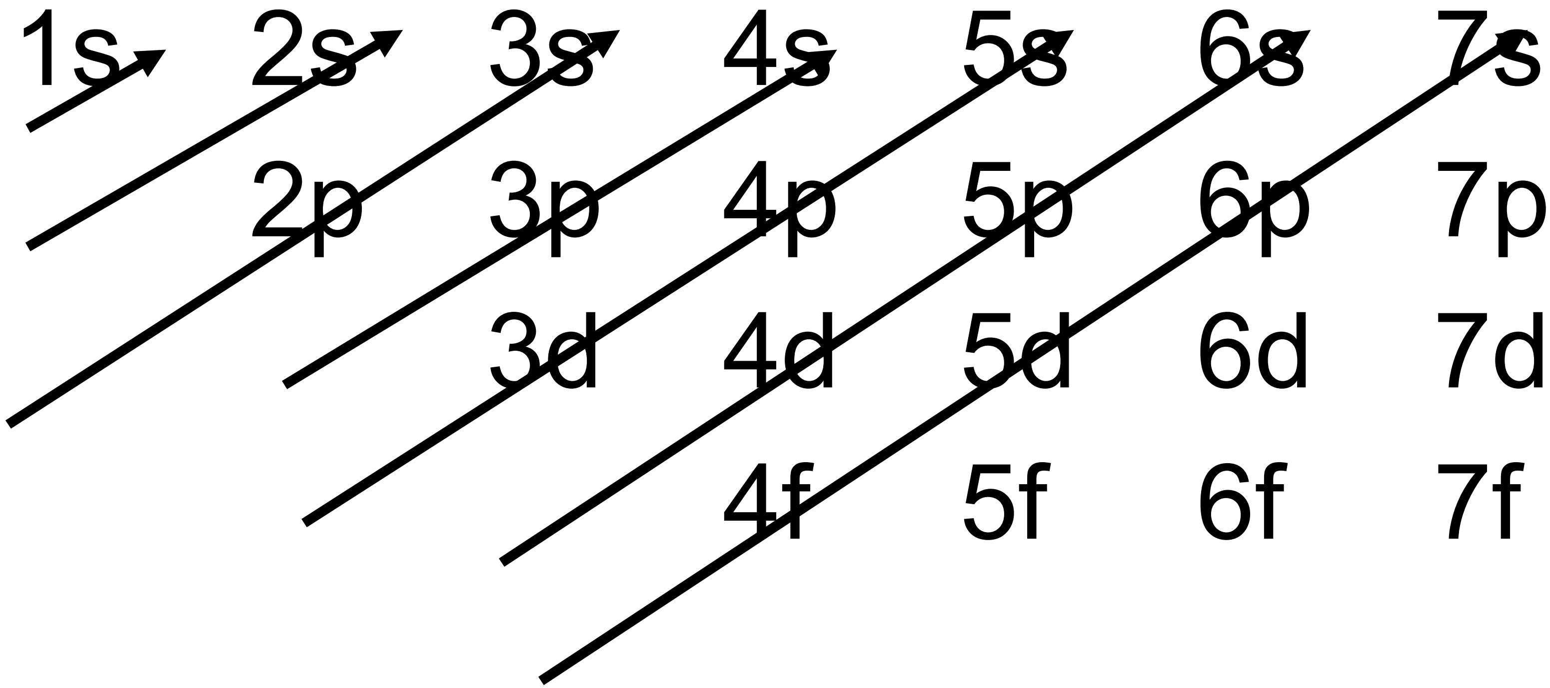


Shell and subshell capacities





The Diagonal Rule for Configurations



If n+l is same, fill the configuration with smaller n first

if n+l are different and n are same, fill smaller l

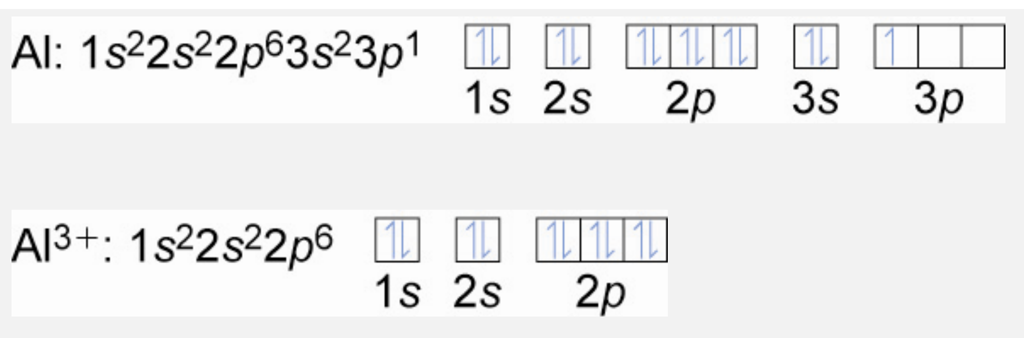
and n is different, fill larger n

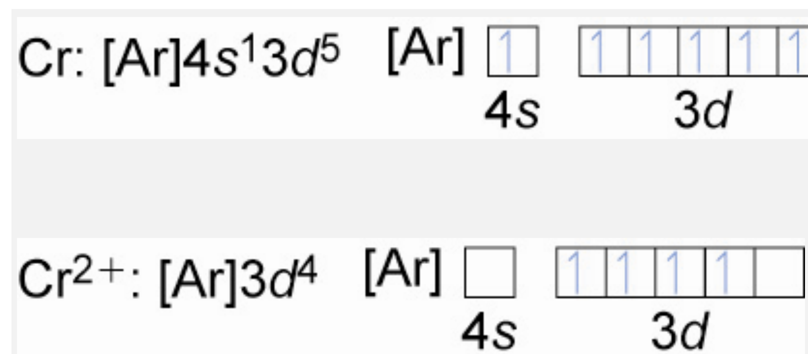
Hund's rules which are empirical state (the first and second) that the term structure with the maximum possible S and the largest possible L for the given S compatible with the Pauli exclusion Principle has the lowest energy.

Hund's third rule (which applies for atoms or ions with a single unfilled shell) states that if the unfilled shell is not more than half-filled the lowest value of J has the lowest energy while if it is more than half-filled the largest value of J has the lowest energy

Hund's rules

Element	Atomic Number	Configuration	Spins of *p* Electrons		
Boron	5	$1s^2 2s^2 2p^1$	↑		
Carbon	6	$1s^2 2s^2 2p^2$	↑	↑	
Nitrogen	7	$1s^2 2s^2 2p^3$	↑	↑	↑
Oxygen	8	$1s^2 2s^2 2p^4$	↑↓	↑	↑
Fluorine	9	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑
Neon	10	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓





Since separation of energies for states of different J arises from spin-orbit term

$$\langle |J, m_J, L, S| \sum_i \xi_i(r_i)\hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i |J, m_J, L, S\rangle$$
$$= \frac{\zeta(L,S)}{2}[J(J+1) - L(L+1) - S(S+1)]$$

separation between pair of adjacent levels in a fine structure multiplet is proportional to larger of two J values,

$$\Delta_J \propto J(J+1) - (J-1)J = 2J$$

e.g. separation between $^3P_2$ and $^3P_1$, and $^3P_1$ and $^3P_0$ should be in ratio 2:1.

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The Physics of Atoms and Quanta

17.2, 17.3, 17.5, 19.1, 19.4, 19.6, 19.7

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1. Show that the normal Zeeman effect should be observed for transitions between the $^1D_2$ and $^1P_1$ states.

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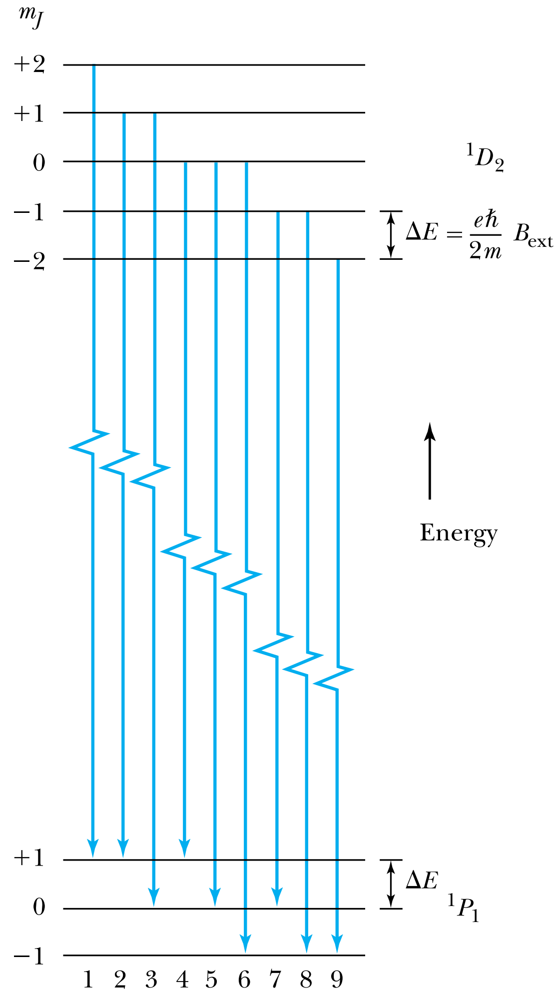

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2. An atom with the states $^2G_{9/2}$ and $^2H_{11/2}$ is placed in a weak magnetic field. Draw the energy levels and indicate the possible allowed transitions between the two states

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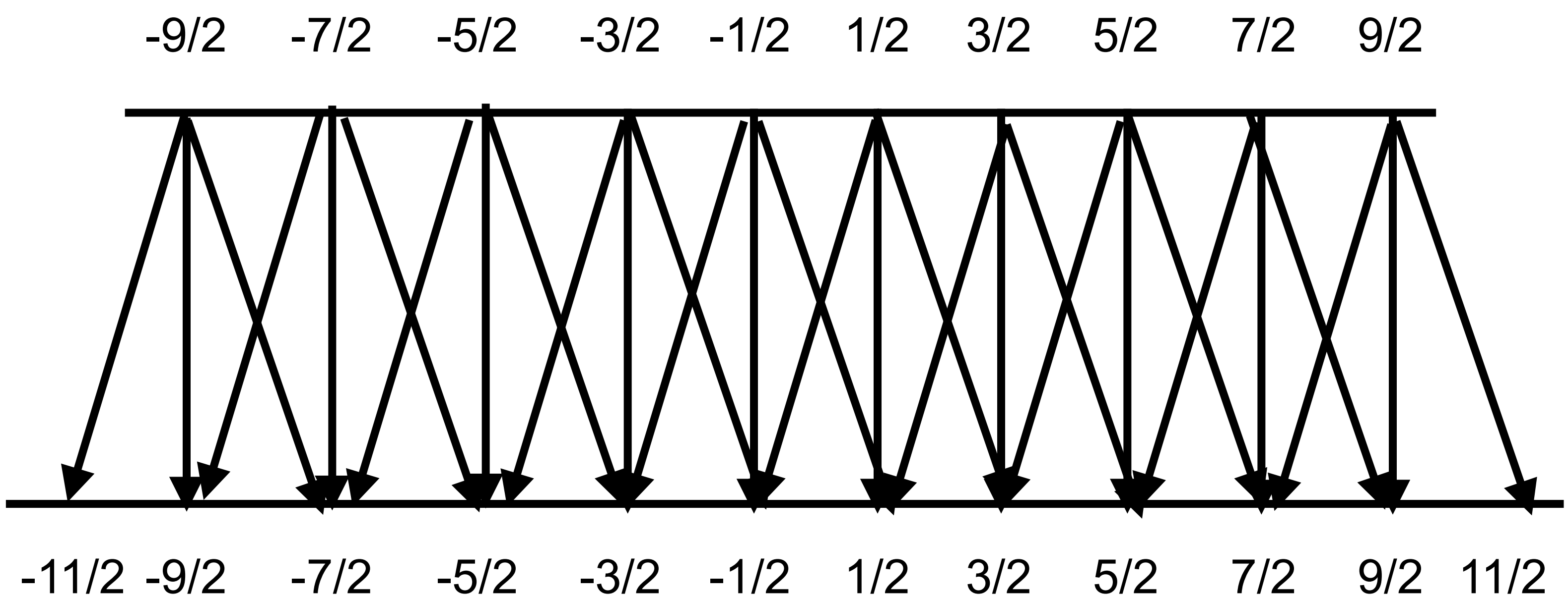

3. Why is it impossible for a $2^2P_{5/2}$ state to exist?

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Solution

A P state has $\mathbf{L} = 1$ and $\mathbf{J} = \mathbf{L} \pm \frac{1}{2}$, so $\mathbf{J} = \frac{5}{2}$ is impossible.

4. The term symbol of the ground state of sodium is $3^2S_{1/2}$ and that of its first excited state is $3^2P_{1/2}$. List the possible quantum numbers n, l, j, and m_l of the outer electron in each case.

4. The term symbol of the ground state of sodium is $3^2S_{1/2}$ and that of its first excited state is $3^2P_{1/2}$. List the possible quantum numbers n, l, j, and m_j of the outer electron in each case.

Solution

$$3^2S_{1/2}\text{: } n=3,\ l=0,\ j=\tfrac{1}{2},\ m_j=\pm\tfrac{1}{2}$$

$$3^2P_{1/2}\text{:}$$

$$n=3,\ l=1,\ j=\tfrac{1}{2},\ m_j=\pm\tfrac{1}{2}$$

5. Consider two electrons in an atom with orbital quantum numbers $l_1=1$ and $l_2=2$. Use LS coupling and find all possible values for the total angular momentum quantum number for J.

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