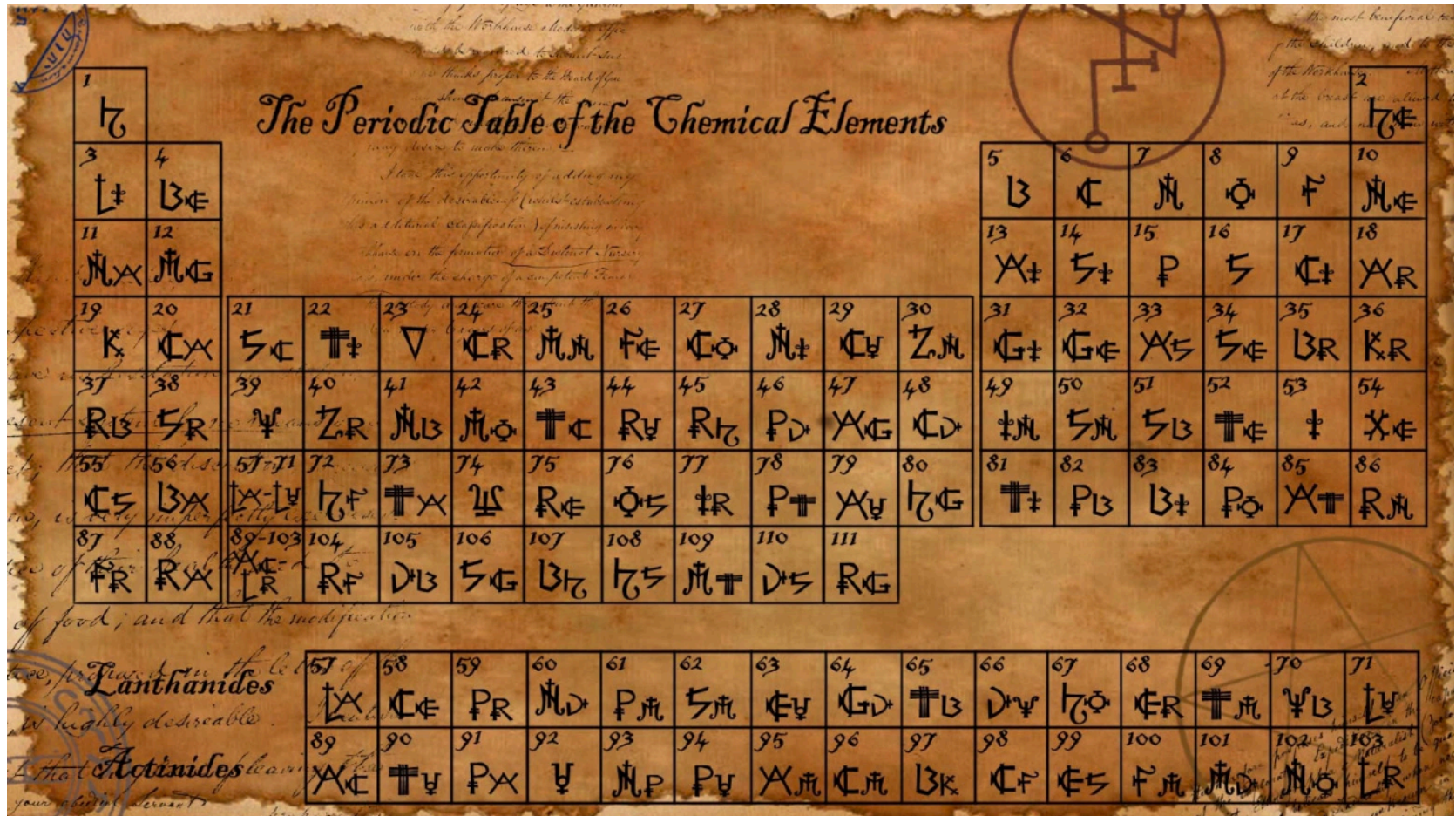




# Atomic Physics

## Chapter 5 Structure of the Periodic system



# The spectra of helium



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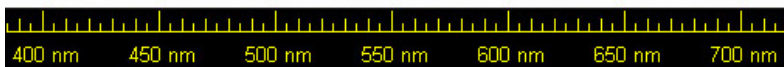
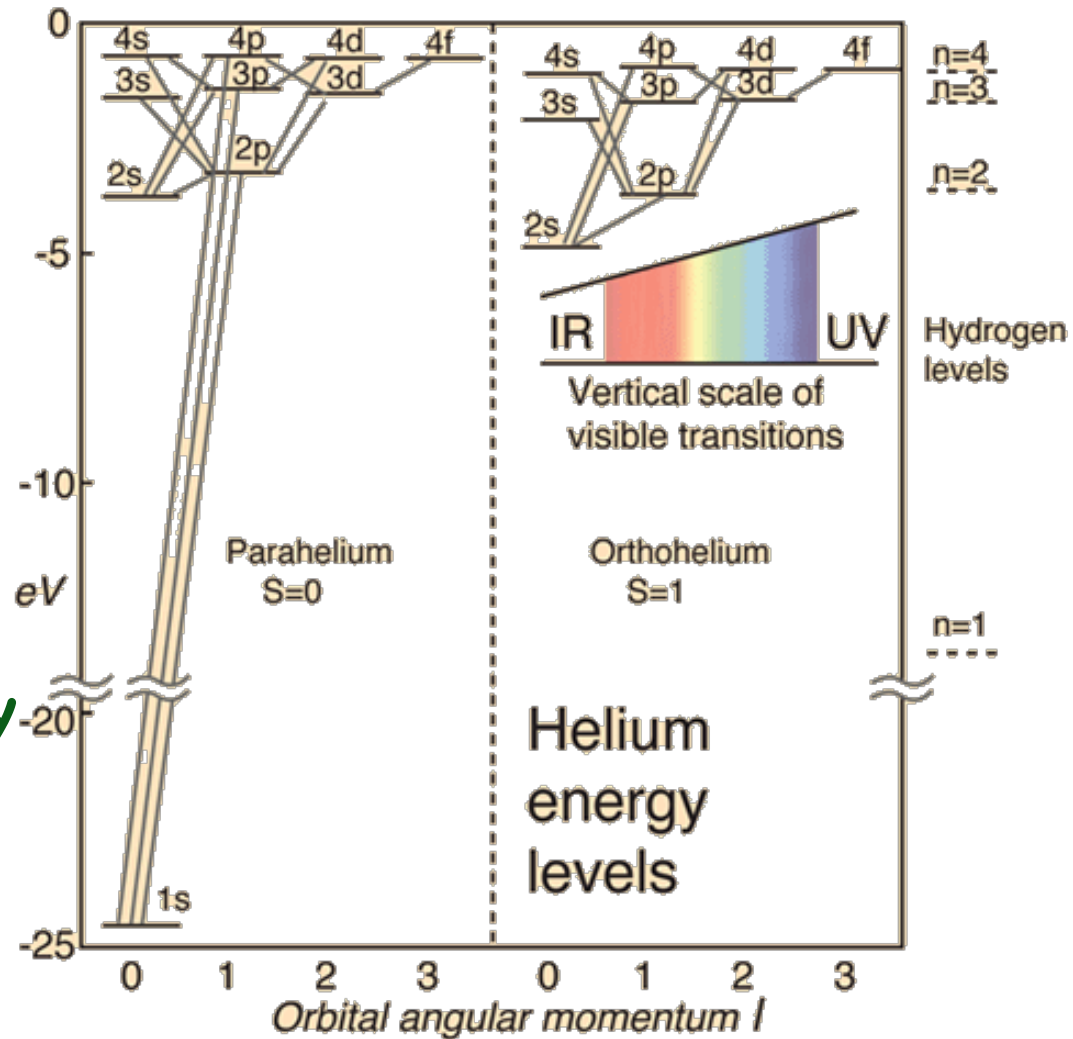
1. Two sets:

parahelium

orthohelium

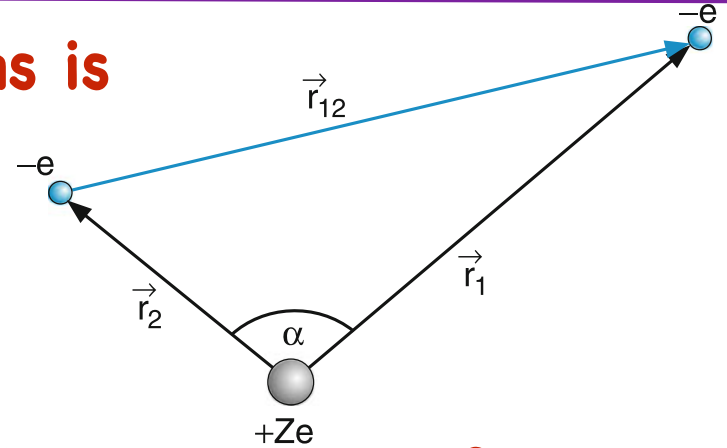
2. Orthohelium has fine structure

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



The potential energy of the electrons is

$$E_{\text{pot}} = -\frac{e^2}{4\pi\epsilon_0} \left( \frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}} \right)$$



The operator of the kinetic energy in the center of mass system is

$$\hat{E}_{\text{kin}} = -\frac{\hbar^2}{2\mu} (\Delta_1(\mathbf{r}_1) + \Delta_2(\mathbf{r}_2))$$

$$\text{with } \mu = \frac{m_e m_K}{m_e + m_K}$$

The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \Delta_1 \psi(\mathbf{r}_1, \mathbf{r}_2) - \frac{\hbar^2}{2m} \Delta_2 \psi(\mathbf{r}_1, \mathbf{r}_2) + E_{\text{pot}} \psi(\mathbf{r}_1, \mathbf{r}_2) = E \psi(\mathbf{r}_1, \mathbf{r}_2).$$

with approximation

$$\mu \approx m_e = m$$

The relative distance

$$r_{12}^2 = |\mathbf{r}_1 - \mathbf{r}_2|^2 = r_1^2 + r_2^2 - 2r_1r_2 \cos \alpha.$$

Therefore, this Schrödinger equation is no longer solvable analytically and we have to use approximations.

Because of the mutual repulsion, the charge distribution of the electrons will be such, that the total energy becomes a minimum. This means: The sum of kinetic energy and potential energy, due to electron-electron repulsion and attraction between the electrons and the nucleus becomes a minimum. On the time average is  $\langle r_{12} \rangle > \langle r_1 \rangle = \langle r_2 \rangle$

# The approximation solutions



In a first crude approximation we can therefore neglect the last term in potential energy. Then we can separate the wave function into the product

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$$

Inserting this into the Schrödinger equation yields two separate equations for the two electrons

$$\begin{aligned} -\frac{\hbar^2}{2m}\Delta_1\psi_1(\mathbf{r}_1) - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r_1}\psi_1(\mathbf{r}_1) &= E_1\psi_1(\mathbf{r}_1) \\ -\frac{\hbar^2}{2m}\Delta_2\psi_2(\mathbf{r}_2) - \frac{e^2}{4\pi\epsilon_0}\frac{Z}{r_2}\psi_2(\mathbf{r}_2) &= E_2\psi_2(\mathbf{r}_2) \end{aligned}$$

with

$$E_1 + E_2 = E$$

# The approximation solutions



With  $Z = 2$  we obtain in this approximation for the total energy of the two electrons in the lowest state with  $n = 1$ :

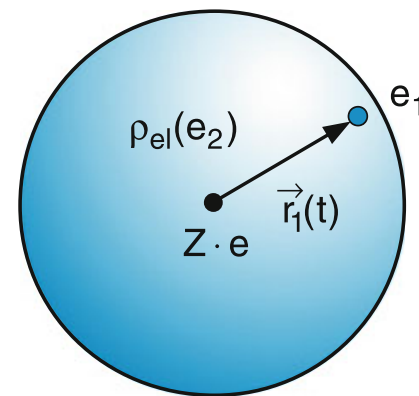
$$\begin{aligned} E_{\text{He}}(1s) &= -2Z^2 E_{\text{H}} = -2 \cdot 4 \cdot 13.6 \text{ eV} \\ &= -108.8 \text{ eV}. \end{aligned}$$

The experimental value for this energy that is necessary to remove both electrons from the atom (this means to convert the He atom into the doubly charged ion  $\text{He}^{++}$ ) is, however, only  $E_{\text{exp}} = 78.98 \text{ eV}$ . The neglect of the electron repulsion therefore introduces an absolute error of 30 eV, i.e., a relative error of about 40%.

# The approximation solutions

A much better approximation is obtained by a model that assumes that each of the two electrons moves in the Coulomb potential of the nucleus, shielded by the charge distribution of the other electron (which is assumed to have a spherically symmetric time average). The resulting potential for each electron is then a spherically symmetric Coulomb potential generated by the effective charge

$$Q_{\text{eff}} = (Z - S)e$$



$$\rho_{\text{el}}(e_2) = -\psi_{1s}^* \cdot \psi_{1s} \cdot e$$

# The approximation solutions



For total shielding  $S = 1$  one would need the energy  $E_H$  to remove the first electron from the atom. The remaining ion  $\text{He}^+$  now has the nuclear charge  $+2e$  and the binding energy of the second electron is therefore  $-Z^2 E_H = -4E_H$ . The total ionization energy of the He atom is then

$$E_{\text{He}}(1s) = -E_H - 4E_H = -5E_H = -68 \text{ eV}$$

which comes much closer to the experimental value  $E_{\text{He}} = -78.983 \text{ eV}$ . For a shielding constant  $S = 0.656$  the experimental value is exactly reproduced. In our model the correct energy is therefore obtained for an effective nuclear charge of  $Z_{\text{eff}} e = +1.344 e$ .



# The coupling of electrons



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

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

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.**

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:

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

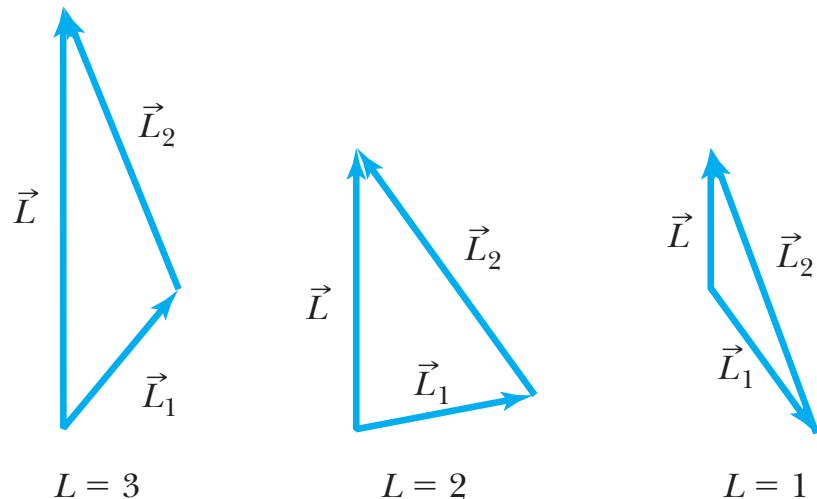
# The coupling of two electrons

## The coupling of two angular momenta

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

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

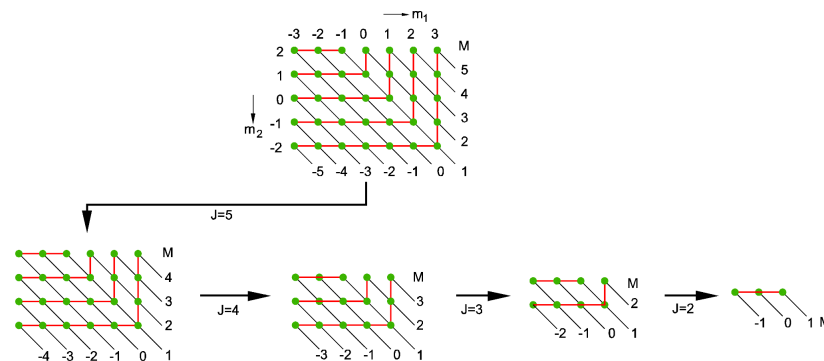
$$L = \sqrt{l(l + 1)}\hbar$$



where,

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

$$m = m_1 + m_2$$



# 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



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

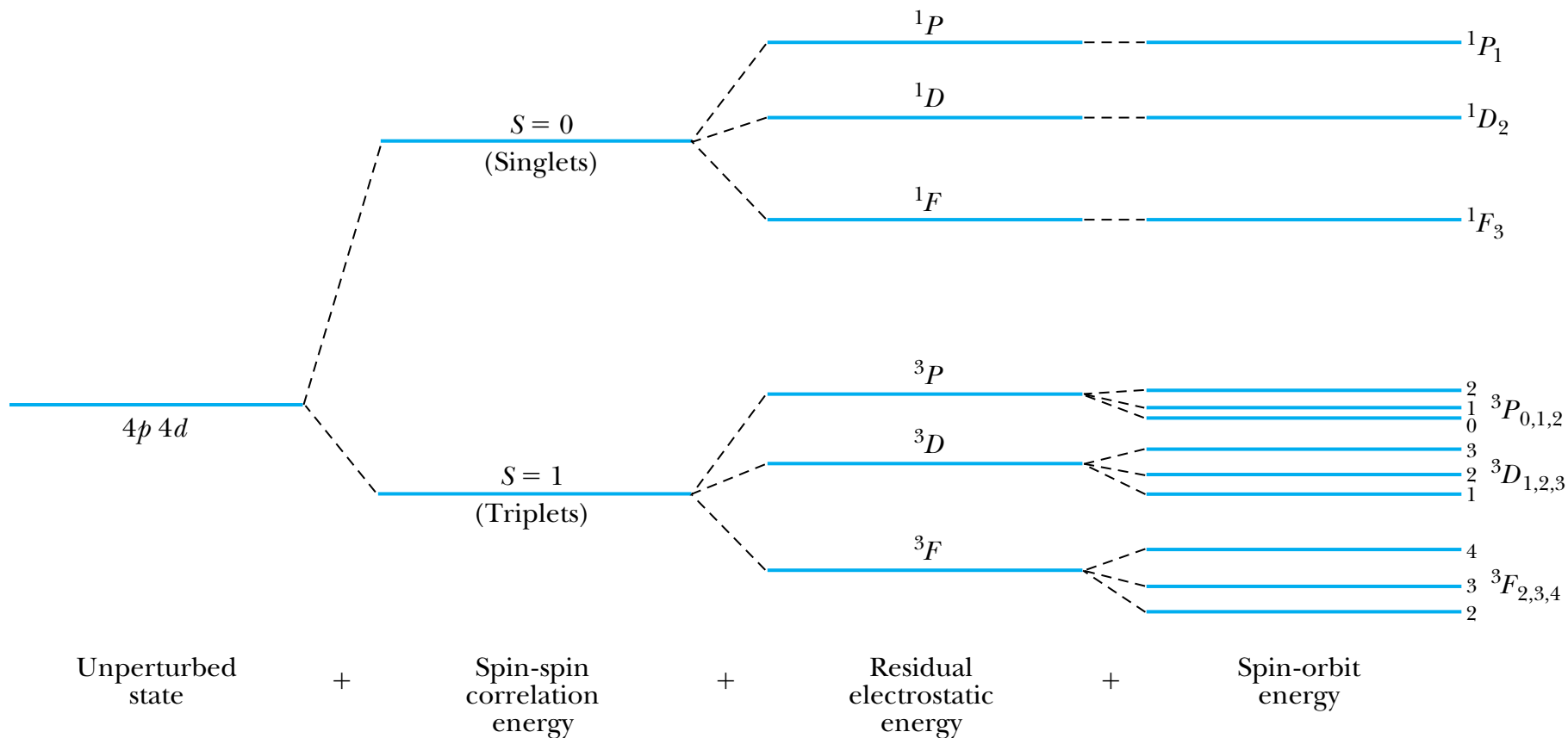
$S$	$L$	$J$	Spectroscopic Symbol
0 (singlet)	1	1	$4^1P_1$
	2	2	$4^1D_2$
	3	3	$4^1F_3$
1 (triplet)	1	2	$4^3P_2$
		1	$4^3P_1$
		0	$4^3P_0$
1 (triplet)	2	3	$4^3D_3$
		2	$4^3D_2$
		1	$4^3D_1$
1 (triplet)	3	4	$4^3F_4$
		3	$4^3F_3$
		2	$4^3F_2$

# The coupling of two electrons



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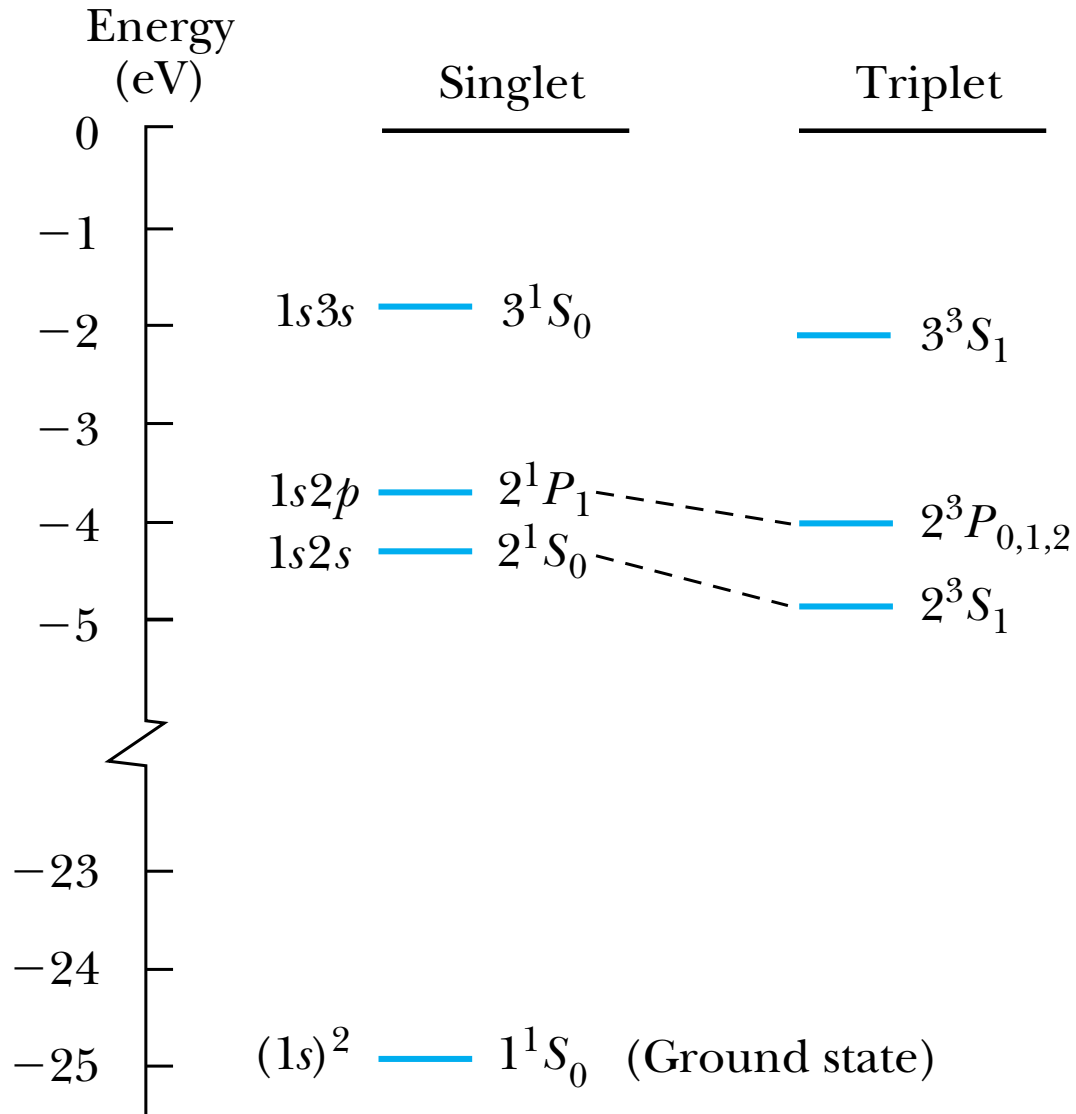
A schematic diagram showing the relative energies of these states appears



# The spectra of helium



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# The coupling of two electrons

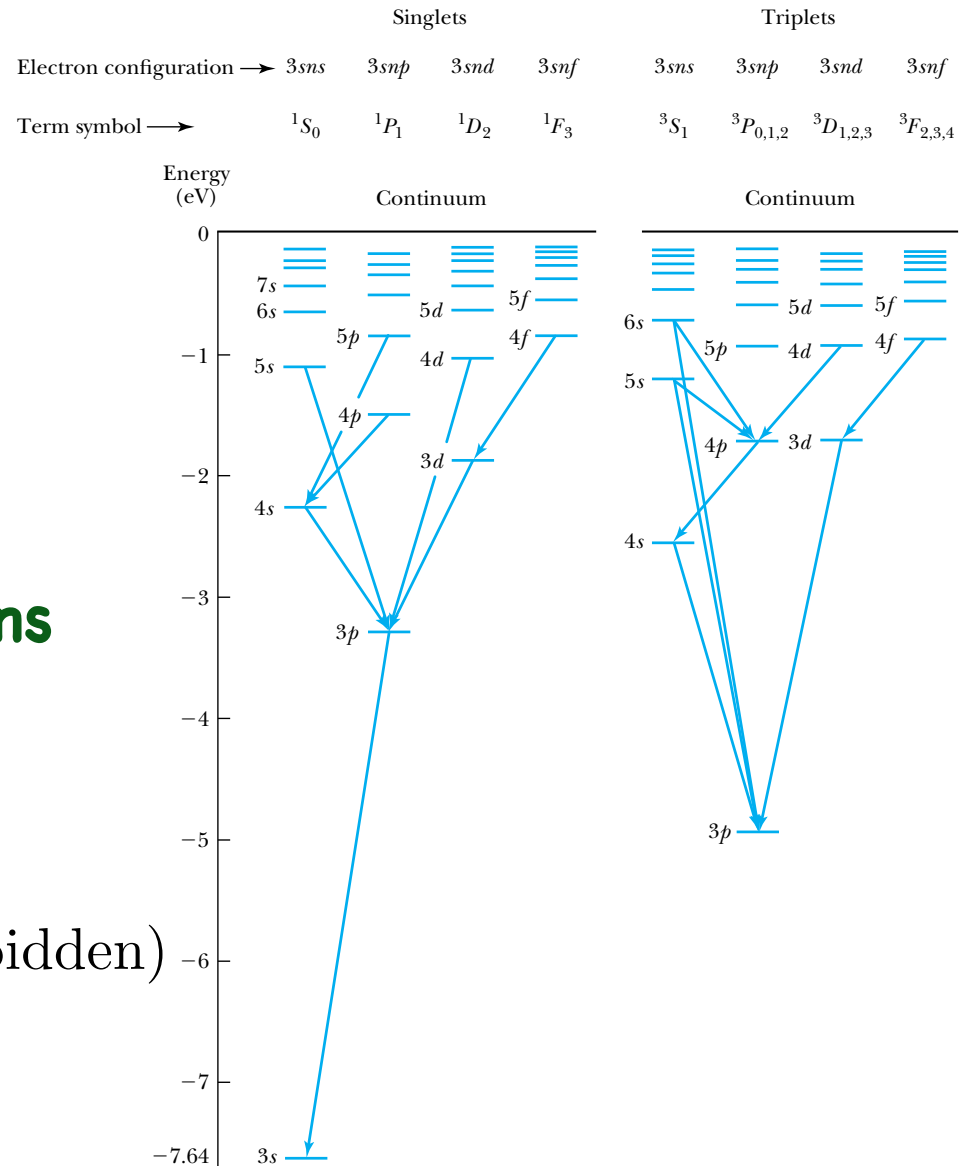


As an example of the optical spectra obtained from two electron atoms, we consider the energy-level diagram of magnesium.

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

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

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





# The coupling of two electrons



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

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

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

The allowed transitions for a single-electron atom are

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

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

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

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

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

The choice rules of transitions for jj coupling are

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

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

The parity requirement

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

## A classical oscillating electric dipole

$$\mathbf{p} = q\mathbf{r} = p_0 \sin \omega t$$

emits the average power, integrated over all directions  $\theta$  against the dipole axis

$$\overline{P} = \frac{2}{3} \frac{\overline{p^2} \omega^4}{4\pi \epsilon_0 c^3} \quad \text{with} \quad \overline{p^2} = \frac{1}{2} p_0^2$$

In analogy to the classical expression for the average dipole moment we define the integral

$$M_{ik} = -e \int \psi_i^* \mathbf{r} \psi_k d\tau$$

as transition dipole moment for a transition between the atomic states,  $i$  and  $k$ .

It follows that for the spontaneously emitted radiation only those transitions  $|i\rangle \rightarrow |k\rangle$  are allowed for which the transition dipole matrix element is not zero. This means that at least one of the components

$$(M_{ik})_x = e \int \psi_i^* x \psi_k d\tau$$

$$(M_{ik})_y = e \int \psi_i^* y \psi_k d\tau$$

$$(M_{ik})_z = e \int \psi_i^* z \psi_k d\tau$$

must be different from zero.

The hydrogenous wave functions are

$$\psi_{n,l,m_l} = \frac{1}{\sqrt{2\pi}} R_{n,l}(r) \Theta_m^l(\vartheta) e^{im_l\varphi}.$$

For linearly polarized light with the electric field vector  $\mathbf{E} = \{0, 0, E_0\}$  only the z-component of  $M_{ik}$  contributes to the spontaneous emission. We choose the z-axis as quantization axis. With  $z = r \cos \theta$  the z-component becomes

$$(M_{ik})_z = \frac{1}{2\pi} \int_{r=0}^{\infty} R_i R_k r^3 dr \times \int_{\vartheta=0}^{\pi} \Theta_{m_k}^{l_k} \Theta_{m_i}^{l_i} \sin \vartheta \cos \vartheta d\vartheta \\ \times \int_{\varphi=0}^{2\pi} e^{i(m_k - m_i)\varphi} d\varphi.$$

For circularly polarized light emitted into the z-direction the x- and y-components of  $M_{ik}$  can contribute to the transition probability. The electric field vector for circularly polarized  $\sigma^+$ -light can be written as  $E^+ = E_x + iE_y$  and for  $\sigma^-$ -light is  $E^- = E_x - iE_y$ .

$$\begin{aligned}
 (M_{ik})_x + i(M_{ik})_y &= \frac{1}{2\pi} \int_{r=0}^{\infty} R_i R_k r^3 dr & (M_{ik})_x - i(M_{ik})_y &= \frac{1}{2\pi} \int_{r=0}^{\infty} R_i R_k r^3 dr \\
 &\times \int_{\vartheta=0}^{\pi} \Theta_{m_i}^{l_i} \Theta_{m_k}^{l_k} \sin^2 \vartheta d\vartheta & &\times \int_{\vartheta=0}^{\pi} \Theta_{m_i}^{l_i} \Theta_{m_k}^{l_k} \sin^2 \vartheta d\vartheta \\
 &\times \int_{\varphi=0}^{2\pi} e^{i(m_k - m_i + 1)\varphi} d\varphi & &\times \int_{\varphi=0}^{2\pi} e^{i(m_k - m_i - 1)\varphi} d\varphi.
 \end{aligned}$$

$$x = r \sin \vartheta \cos \varphi \quad y = r \sin \vartheta \sin \varphi$$

# Pauli exclusion principle



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

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

## 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



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



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



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The ground state of Helium

The size of atom

The atom of metal

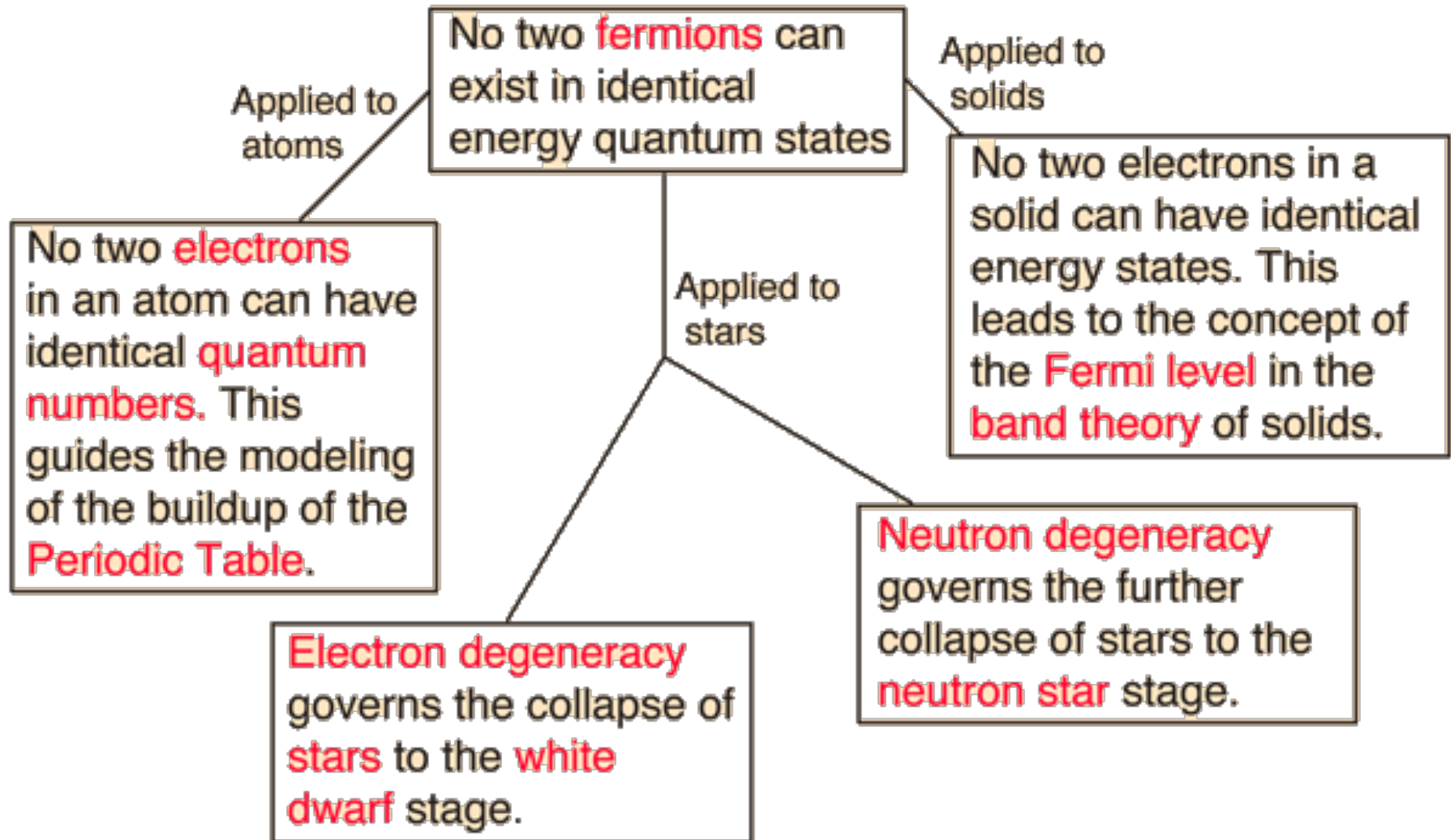
The independent motion of nucleon

The colors of quarks

# The applications



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# The equivalent electrons

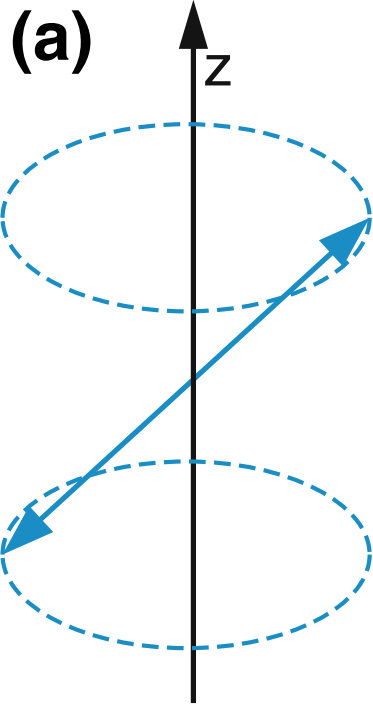


Equivalent electrons: those which belong to same  $(n,l)$  subshells

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

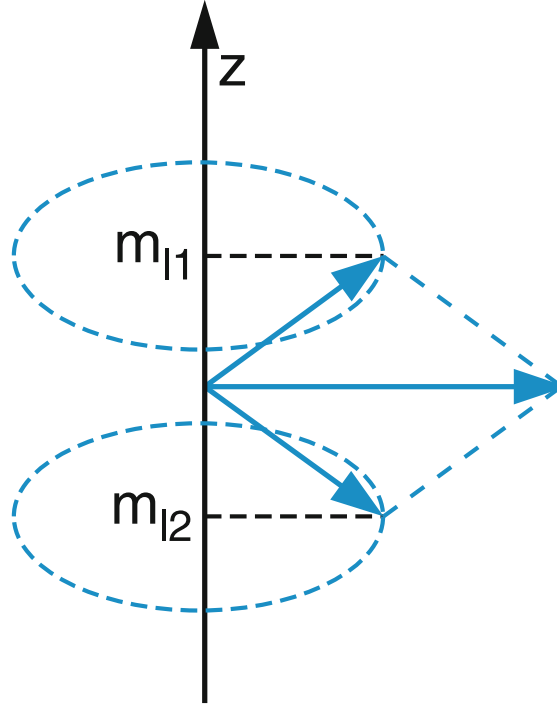
	$m$												
$np^2$	1	↑↓			↑		↑	↑		↑	↑		↓
	0		↑↓		↓	↑		↑	↑		↓	↓	
	-1			↑↓		↓	↓		↑	↑		↑	↑
	$M_L$	2	0	-2	1	-1	0	1	0	-1	1	0	-1
	$M_S$	0	0	0	0	0	0	1	1	1	0	0	0
		⏟					⏟		⏟				
		${}^1D_2$					${}^1S_0$		${}^3P_{2,1,0}$				

## Vector model of the $p^2$ configuration



$$L=0, m_{l_1}=1, m_{l_2}=-1$$

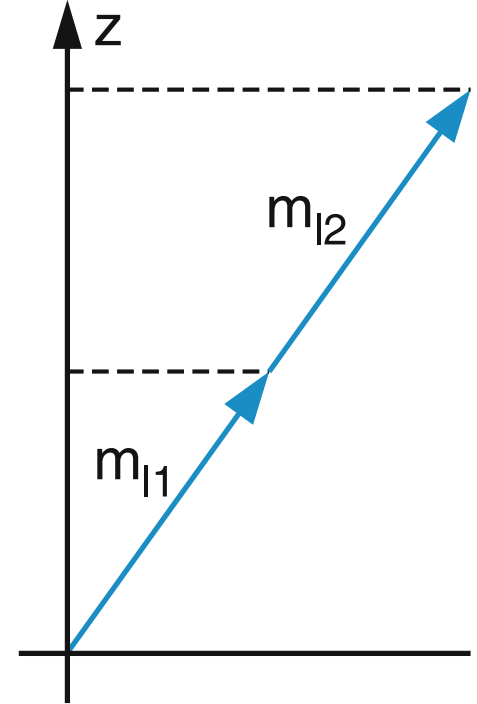
S term



$$L=1, m_{l_1}=1, m_{l_2}=-1$$

$$M=0$$

P term

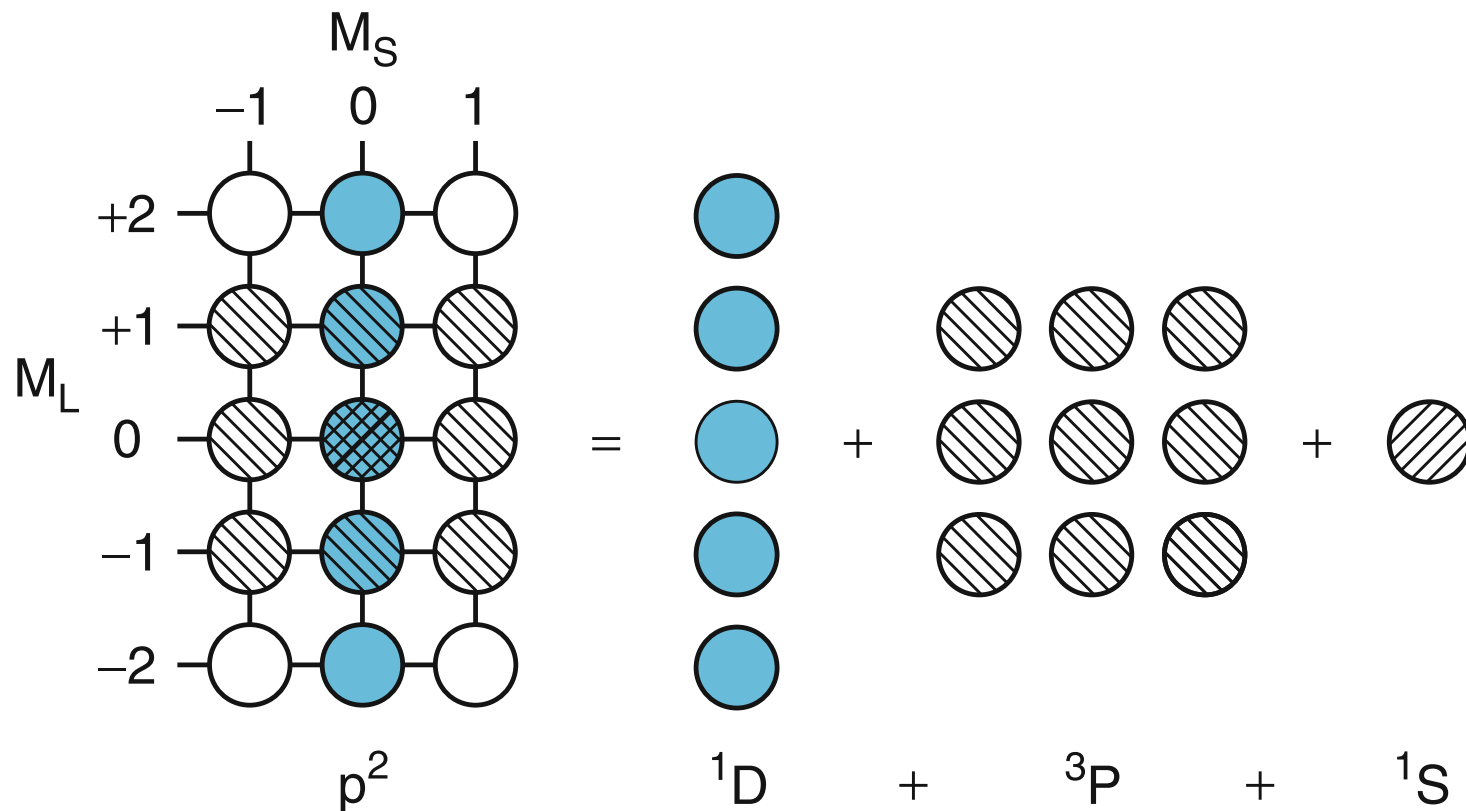


$$L=2, m_{l_1}=m_{l_2}=+1$$

$$M=2$$

D term

## Slater diagram



# The equivalent electrons



## Possible total angular momenta and resulting atomic levels for different two-electron configurations

Electron configuration	Quantum numbers of angular momenta			Level assignment
	$L$	$S$	$J$	
$s$	0	$\frac{1}{2}$	$\frac{1}{2}$	$^2S_{1/2}$
$s^2$	0	0	0	$^1S_0$
	0	1	1	$^3S_1$ for $n_1 \neq n_2$
$sp$	1	0	1	$^1P_1$
	1	1	0, 1, 2	$^3P_0, ^3P_1, ^3P_2$
$p^2$	0	0	0	$^1S_0$
	1	1	0, 1, 2	$^3P_0, ^3P_1, ^3P_2$
	2	0	2	$^1D_2$
	0	1	1	$^3S_1$
				$^1P_1$
				$^3D_{1,2,3}$
	1	0	1	} <i>only for</i> $n_1 \neq n_2$
2	1	1, 2, 3		



## 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
$d^3 d^7$	$^2P \ ^4P \ ^2D \ ^2F \ ^4F \ ^2G \ ^2H$	V, Co
$d^4 d^6$	$^2^1S \ ^2^3P \ ^2^1D \ ^3D \ ^5D \ ^1F$ $^2^3F \ ^2^1G \ ^3G \ ^3H \ ^1I$	Fe
$d^5$	$^2S \ ^6S \ ^2P \ ^4P \ ^3D \ ^4D \ ^2F$ $^4F \ ^2G \ ^4G \ ^2H \ ^2I$	Mn
$d^{10}$	$^1S$	Zn

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

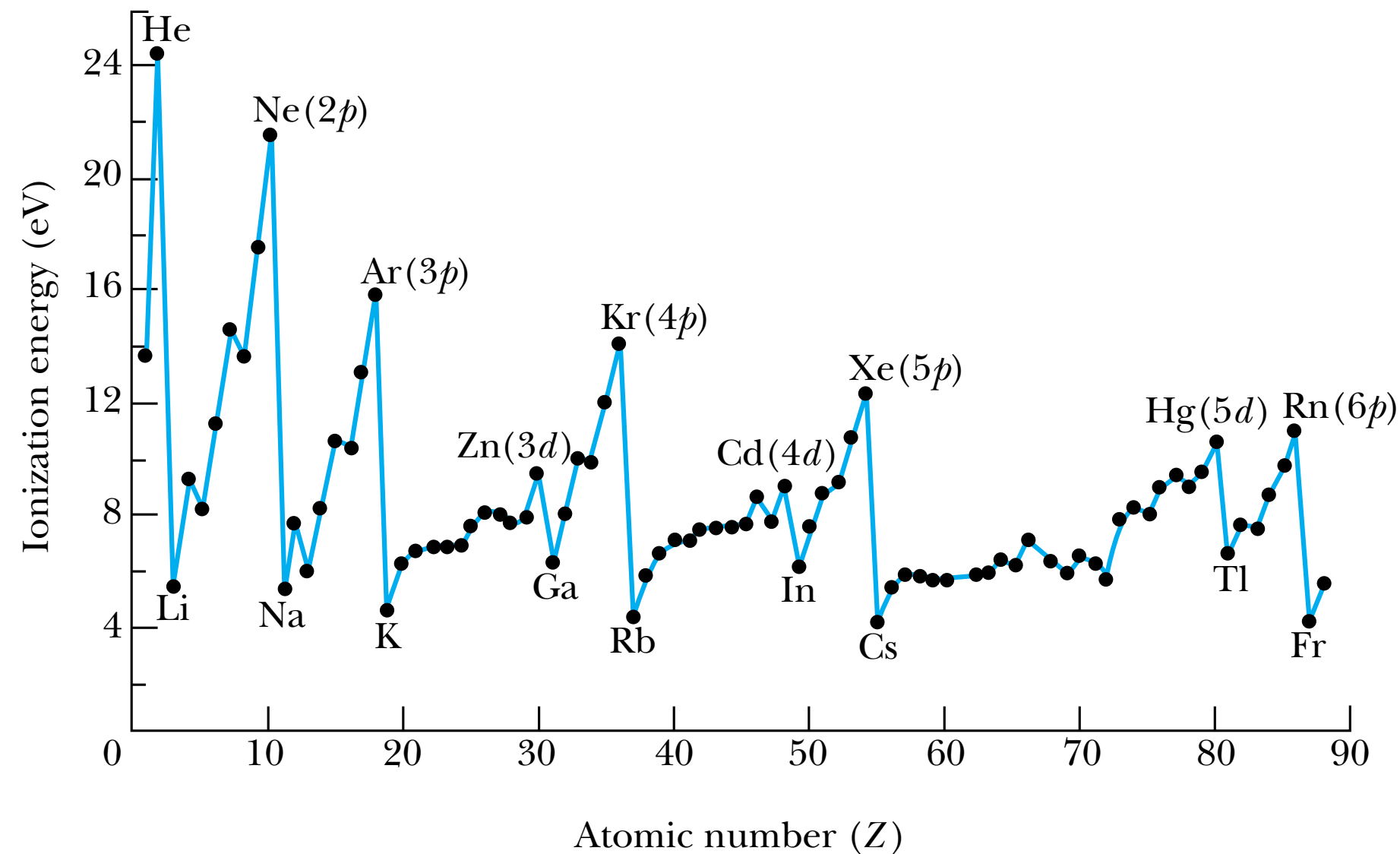
# Periodic Table of Elements



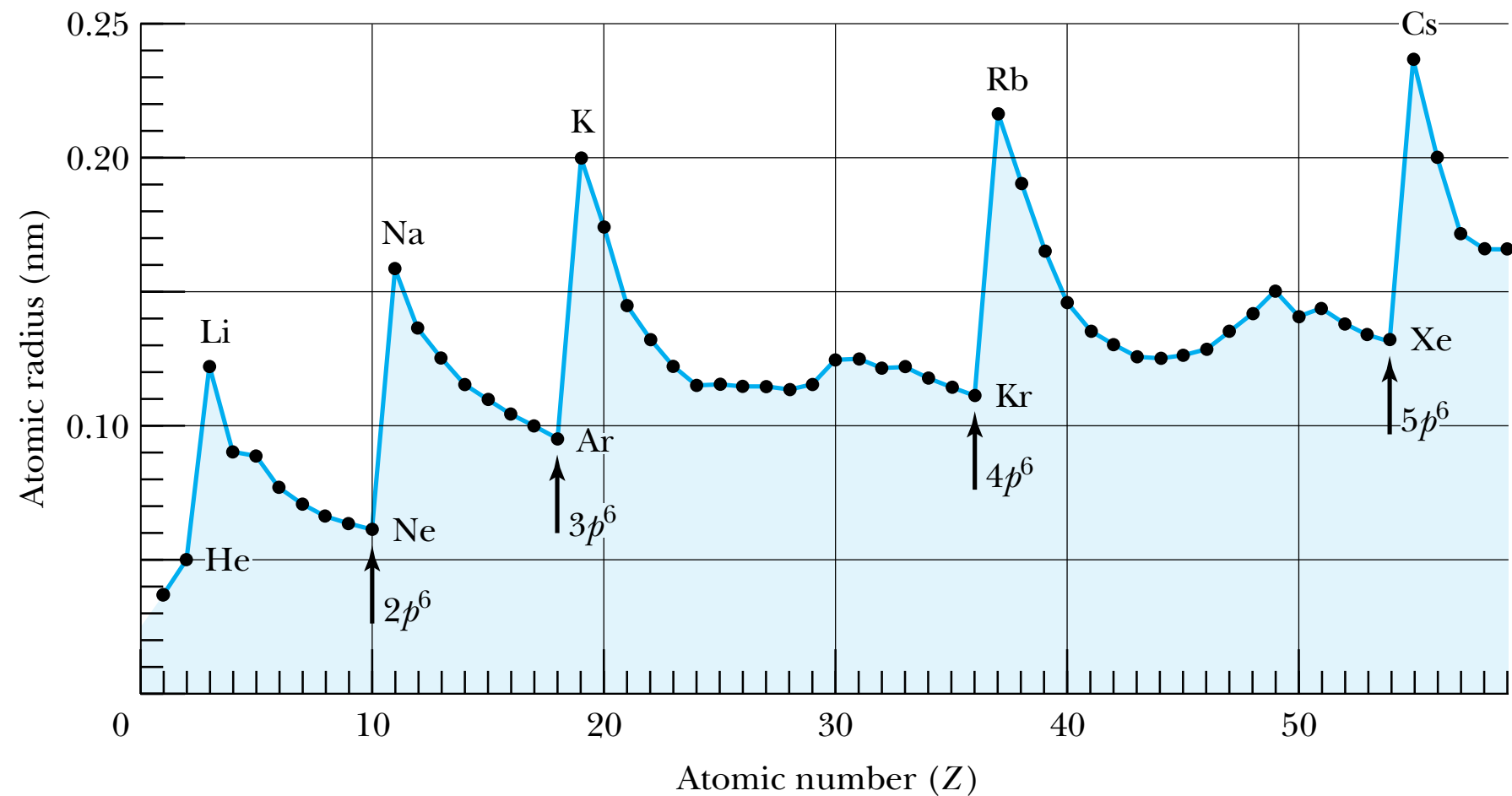
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Closed shells		Alkaline earths										Rare Halogens gases						
Alkalis																		
Groups:	1	2	Transition elements										13	14	15	16	17	18
	1																	2
	H																	He
	$1s$																	$1s^2$
$1s^2$	3	4											5	6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

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



# Atomic radii



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

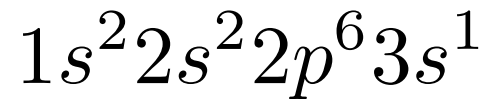
1. The electrons in an atom tend to occupy the lowest energy levels available to them.
2. Only one electron can be in a state with a given (complete) set of quantum numbers (Pauli exclusion principle).

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**.

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

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



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



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

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

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

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

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.



# Explaining the Periodic Table

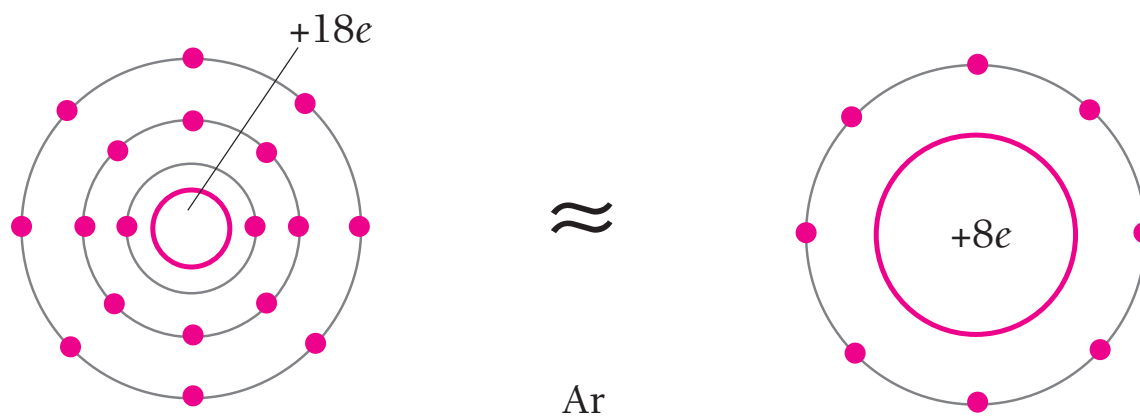
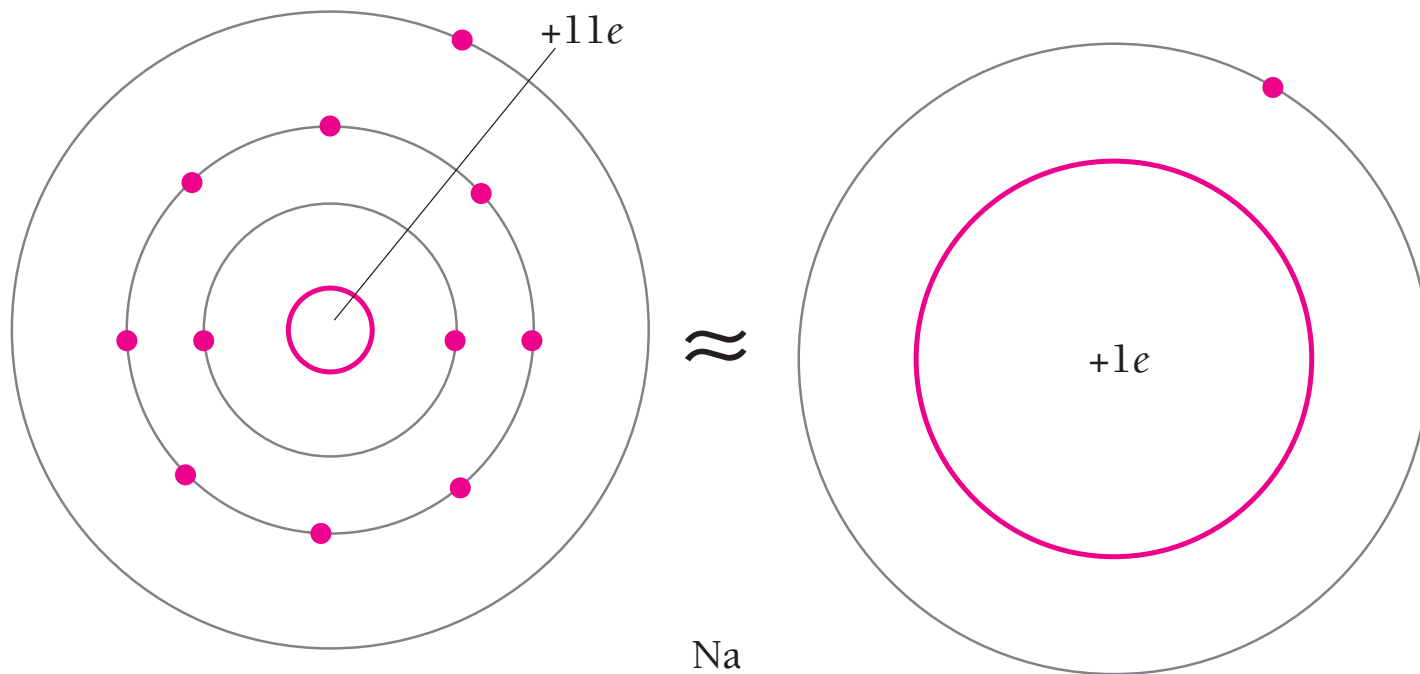


An atomic shell or subshell that contains its full quota of electrons is said to be closed. A closed s subshell ( $l=0$ ) holds two electrons, a closed p subshell ( $l=1$ ) six electrons, a closed d subshell ( $l=2$ ) ten electrons, and so on.

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

# Explaining the Periodic Table

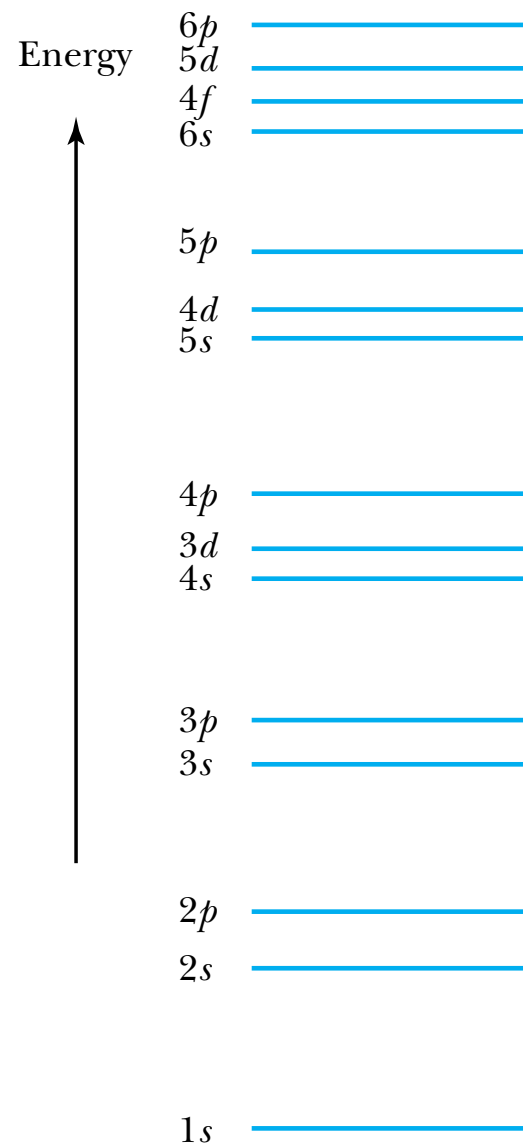


# Shell and subshell capacities



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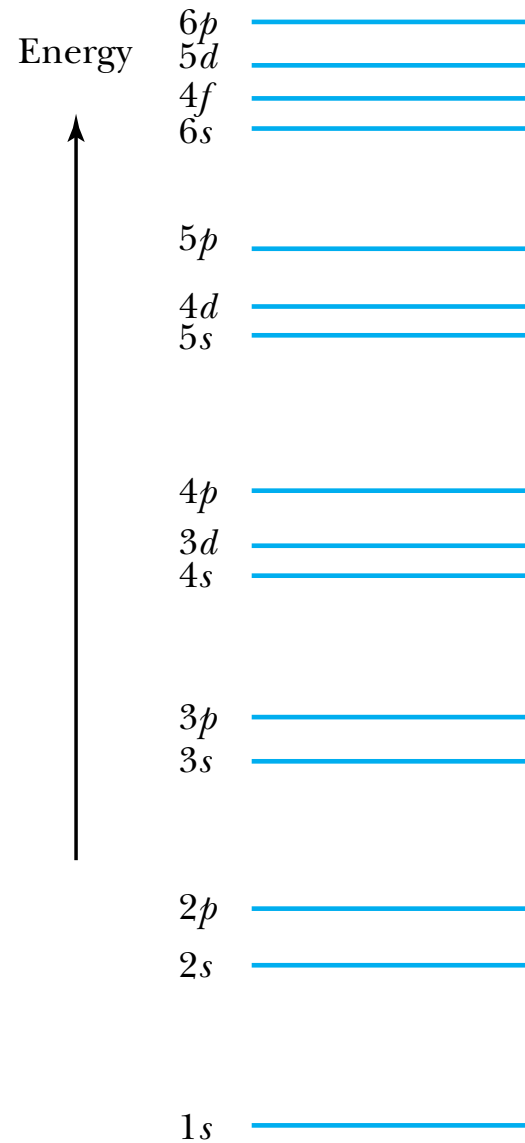
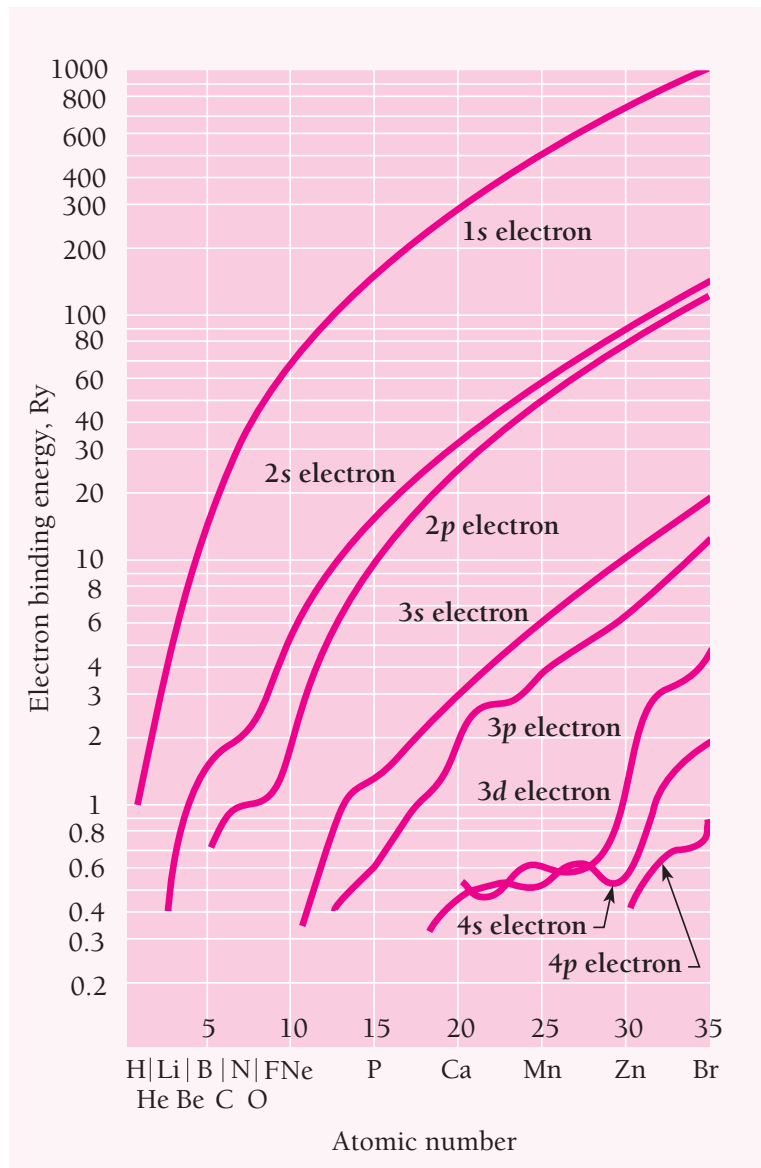
$n$	$\ell$	Subshell	Subshell Capacity	Total Electrons in All Subshells
1	0	1s	2	2
2	0	2s	2	4
2	1	2p	6	10
3	0	3s	2	12
3	1	3p	6	18
4	0	4s	2	20
3	2	3d	10	30
4	1	4p	6	36
5	0	5s	2	38
4	2	4d	10	48
5	1	5p	6	54
6	0	6s	2	56
4	3	4f	14	70
5	2	5d	10	80
6	1	6p	6	86
7	0	7s	2	88
5	3	5f	14	102
6	2	6d	10	112



# Shell and subshell capacities



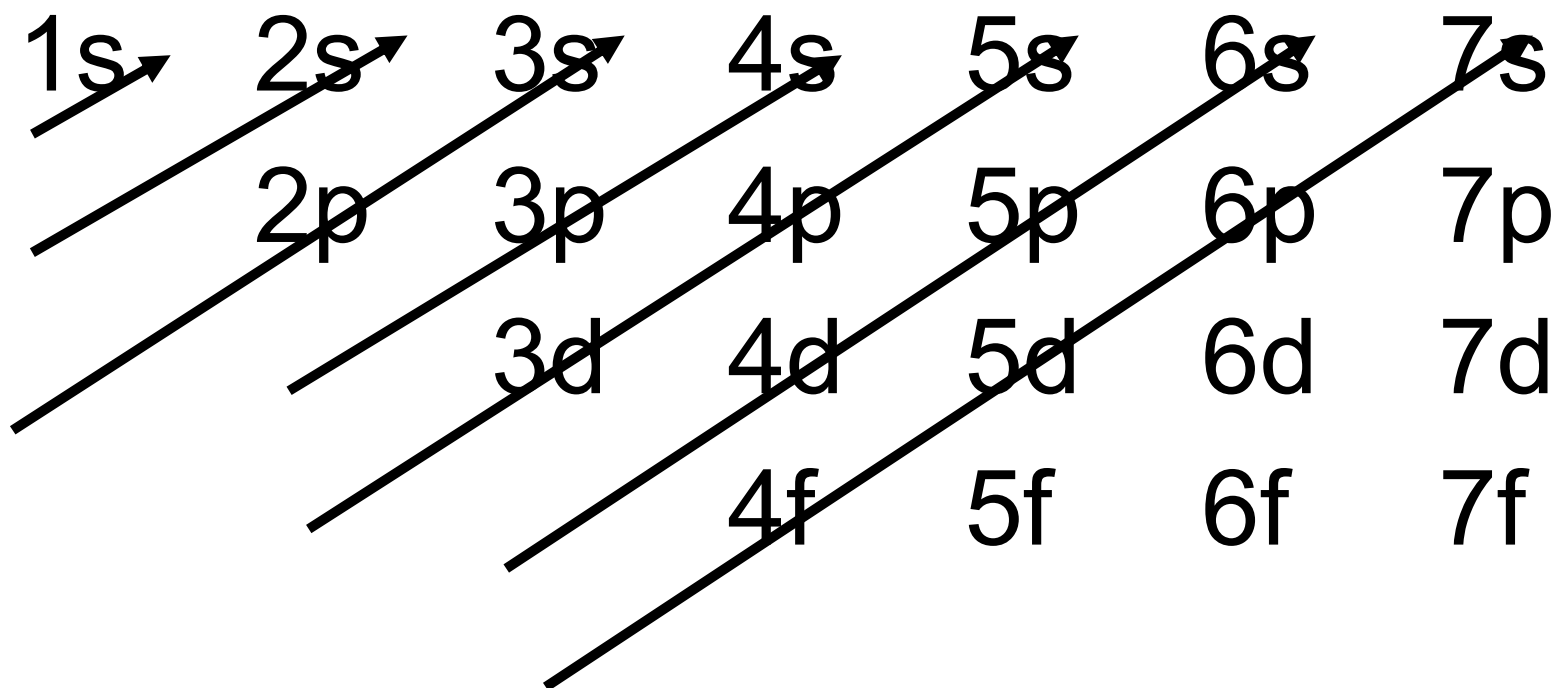
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# The Diagonal Rule for Configurations



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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  $n$

# The Diagonal Rule for Configurations



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Shell				K	L			M			O	Shell				K	L			M			N		O	
Z		Element	1s	2s	2p	3s	3p	3d	4s	Z		Element	1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	5p			
1	H	Hydrogen	1							28	Ni	Nickel	2	2	6	2	6	8	2							
2	He	Helium	2							29	Cu	Copper	2	2	6	2	6	10	1							
3	Li	Lithium	2	1						30	Zn	Zinc	2	2	6	2	6	10	2							
4	Be	Beryllium	2	2						31	Ga	Gallium	2	2	6	2	6	10	2	1						
5	B	Boron	2	2	1					32	Ge	Germanium	2	2	6	2	6	10	2	2						
6	C	Carbon	2	2	2					33	As	Arsenic	2	2	6	2	6	10	2	3						
7	N	Nitrogen	2	2	3					34	Se	Selenium	2	2	6	2	6	10	2	4						
8	O	Oxygen	2	2	4					35	Br	Bromium	2	2	6	2	6	10	2	5						
9	F	Fluorine	2	2	5					36	Kr	Krypton	2	2	6	2	6	10	2	6						
10	Ne	Neon	2	2	6					37	Rb	Rubidium	2	2	6	2	6	10	2	6		1				
11	Na	Sodium	2	2	6	1				38	Sr	Strontium	2	2	6	2	6	10	2	6		2				
12	Mg	Magnesium	2	2	6	2				39	Y	Yttrium	2	2	6	2	6	10	2	6	1	2				
13	Al	Aluminum	2	2	6	2	1			40	Zr	Zirconium	2	2	6	2	6	10	2	6	2	2				
14	Si	Silicon	2	2	6	2	2			41	Nb	Niobium	2	2	6	2	6	10	2	6	4	1				
15	P	Phosphorus	2	2	6	2	3			42	Mo	Molybdenum	2	2	6	2	6	10	2	6	5	1				
16	S	Sulfur	2	2	6	2	4			43	Tc	Technetium	2	2	6	2	6	10	2	6	6	1				
17	Cl	Chlorine	2	2	6	2	5			44	Ru	Ruthenium	2	2	6	2	6	10	2	6	7	1				
18	Ar	Argon	2	2	6	2	6			45	Rh	Rhodium	2	2	6	2	6	10	2	6	8	1				
19	K	Potassium	2	2	6	2	6	1		46	Pd	Palladium	2	2	6	2	6	10	2	6	10					
20	Ca	Calcium	2	2	6	2	6	2		47	Ag	Silver	2	2	6	2	6	10	2	6	10	1				
21	Sc	Scandium	2	2	6	2	6	1	2	48	Cd	Cadmium	2	2	6	2	6	10	2	6	10	2				
22	Ti	Titanium	2	2	6	2	6	2	2	49	In	Indium	2	2	6	2	6	10	2	6	10	2	1			
23	V	Vanadium	2	2	6	2	6	3	2	50	Sn	Tin	2	2	6	2	6	10	2	6	10	2	2			
24	Cr	Chromium	2	2	6	2	6	5	1	51	Sb	Antimony	2	2	6	2	6	10	2	6	10	2	3			
25	Mn	Manganese	2	2	6	2	6	5	2	52	Te	Tellurium	2	2	6	2	6	10	2	6	10	2	4			
26	Fe	Iron	2	2	6	2	6	6	2	53	I	Iodine	2	2	6	2	6	10	2	6	10	2	5			
27	Co	Cobalt	2	2	6	2	6	7	2	54	Xe	Xenon	2	2	6	2	6	10	2	6	10	2	6			

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.

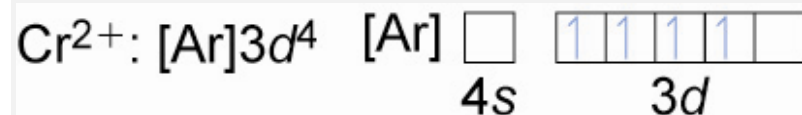
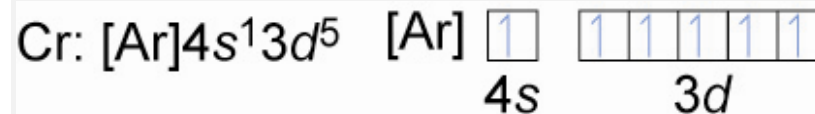
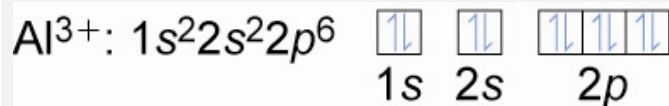
Hund's third rule (which applies for atoms or ions with a single unfilled shell) states that if the unfilled shell is not more than half-filled the lowest value of  $J$  has the lowest energy while if it is more than half-filled the largest value of  $J$  has the lowest energy

# Hund's rules



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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

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

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.

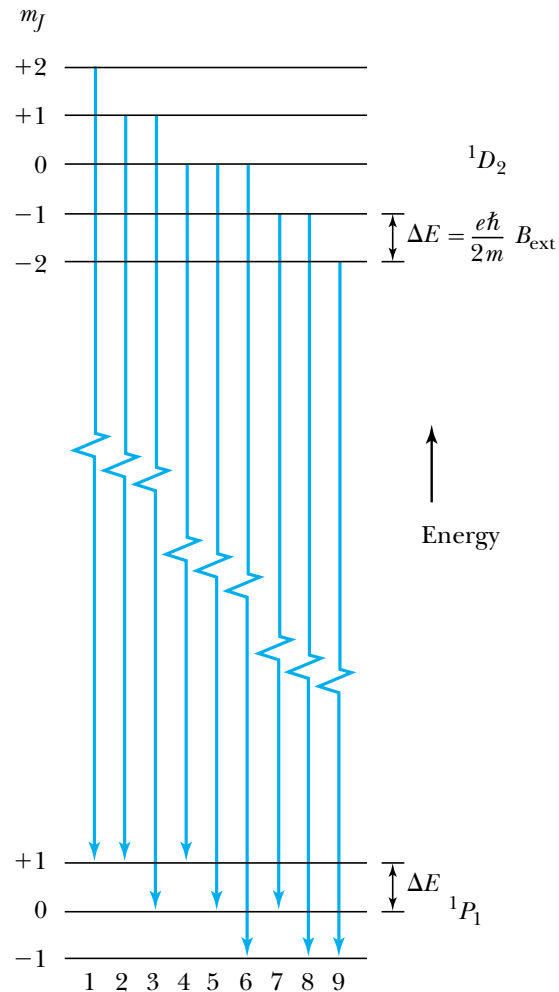
## The Physics of Atoms and Quanta

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



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

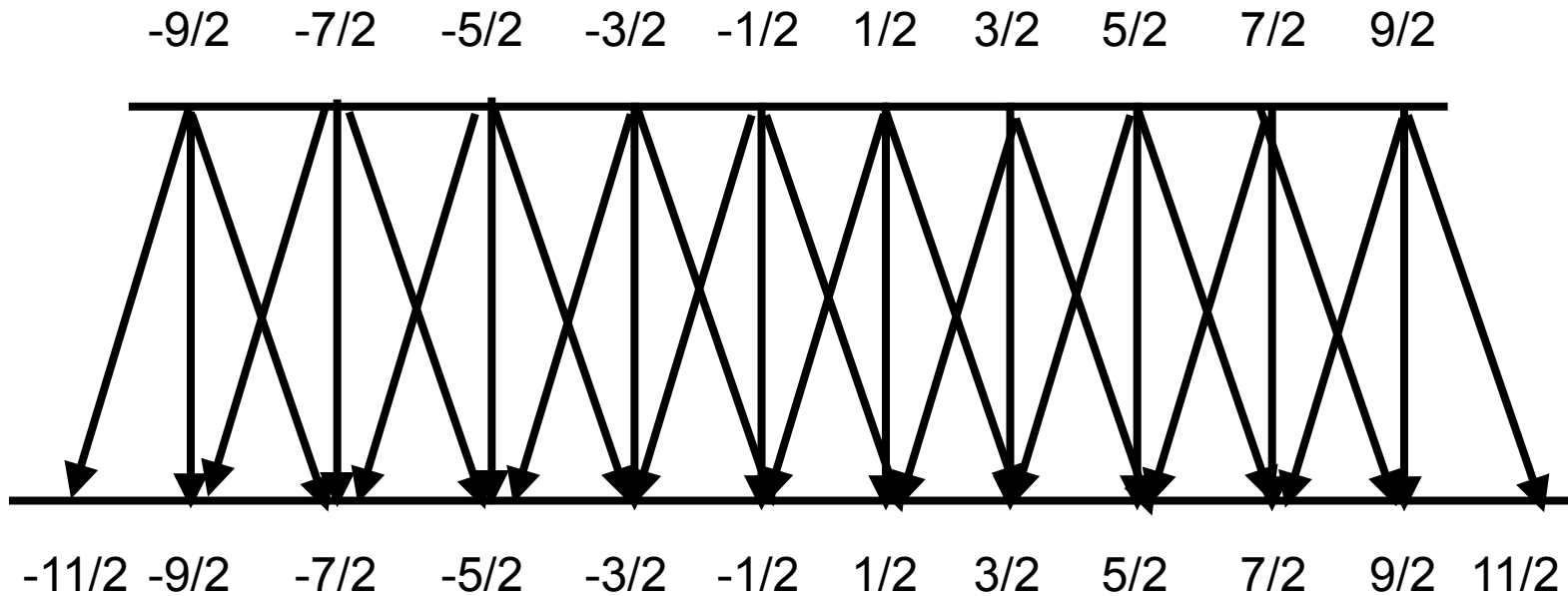
1. Show that the normal Zeeman effect should be observed for transitions between the  $^1D_2$  and  $^1P_1$  states.



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  $L = 1$  and  $J = L \pm \frac{1}{2}$ , so  $J = \frac{5}{2}$  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.

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## Solution

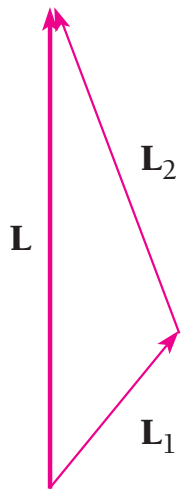
$$3^2S_{1/2}: n = 3, l = 0, j = \frac{1}{2}, m_j = \pm\frac{1}{2}$$

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

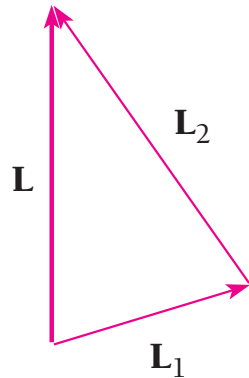
$$n = 3, l = 1, j = \frac{1}{2}, m_j = \pm\frac{1}{2}$$

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.

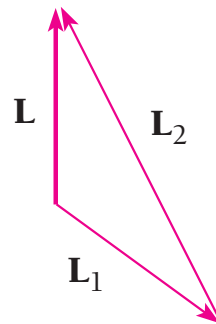
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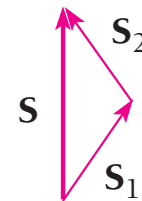
$L = 3$



$L = 2$



$L = 1$



$S = 1$



$S = 0$

(a)

(b)