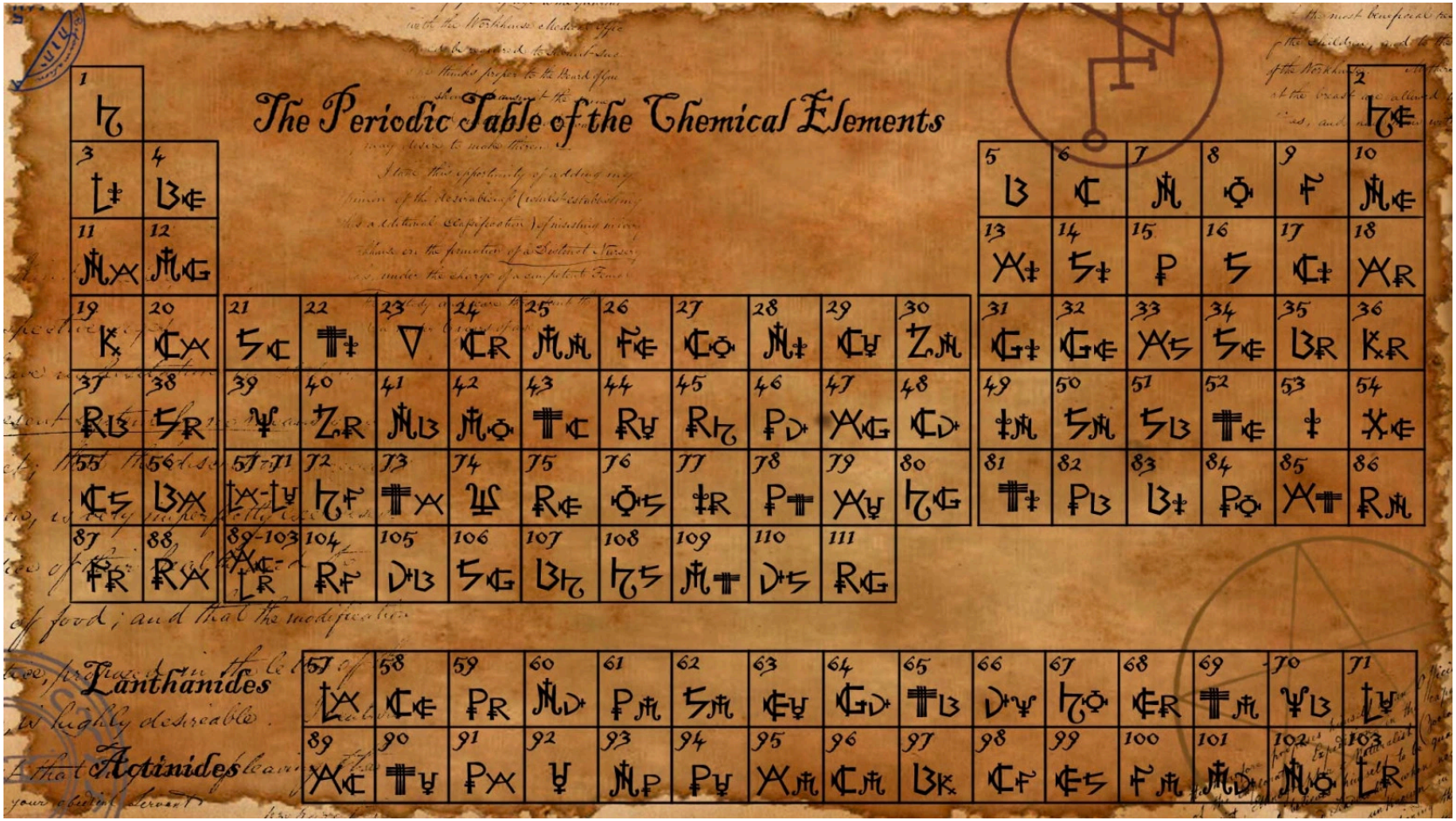
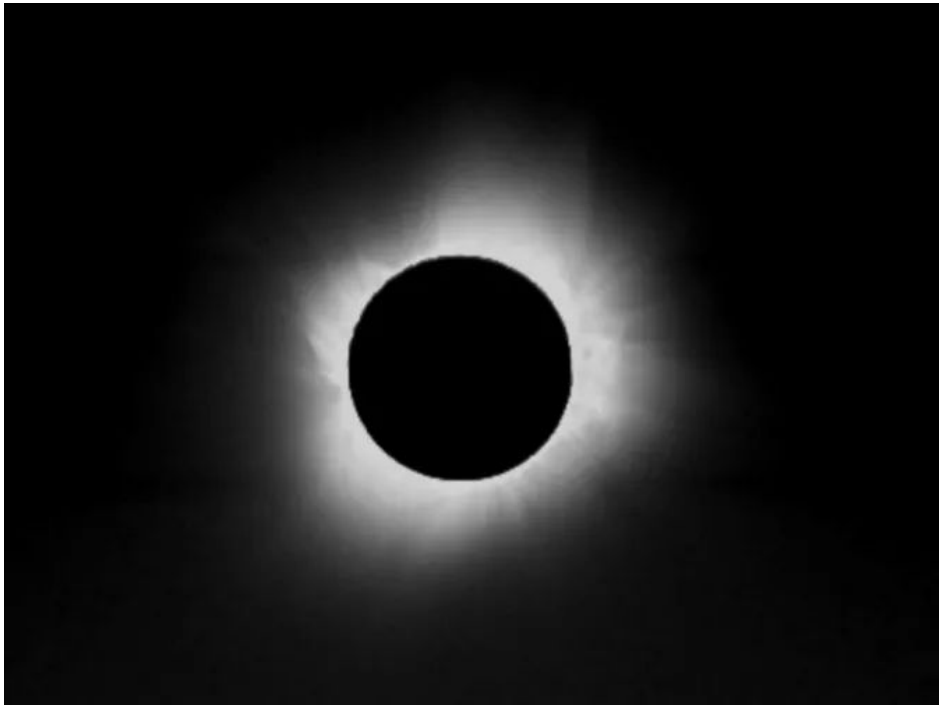
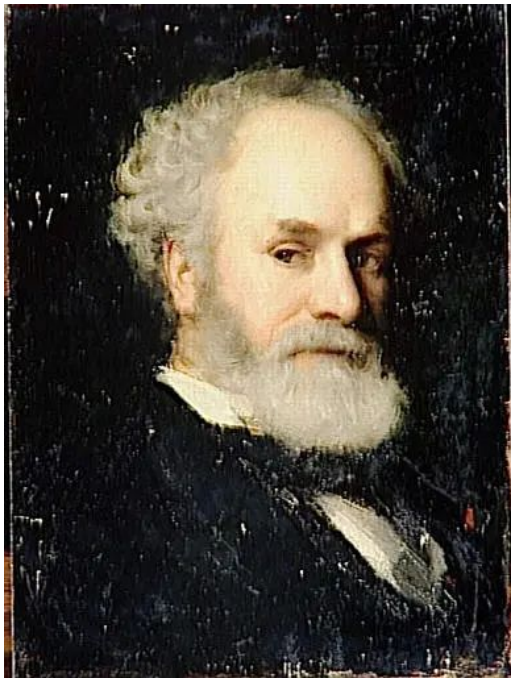
Atomic Physics

Chapter 5 Structure of the Periodic system



The discovery of helium

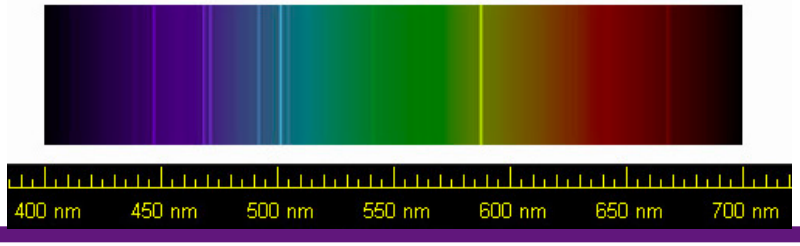


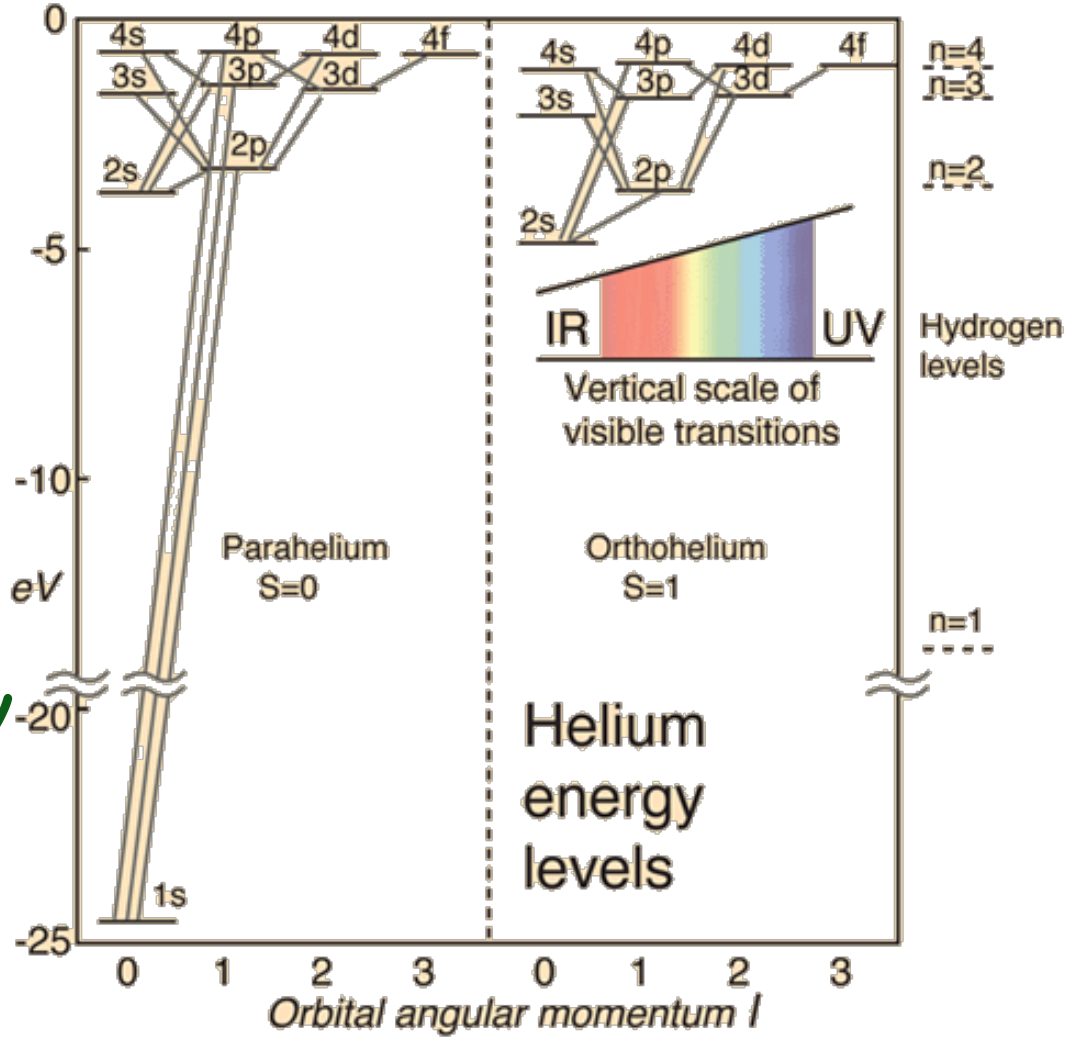




The spectra of helium

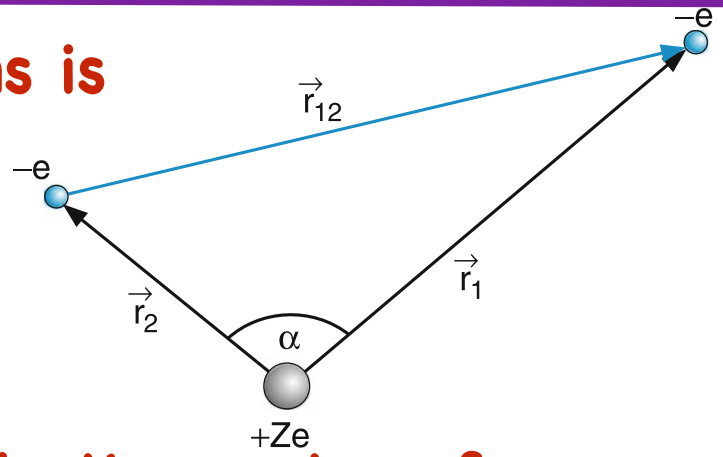
1. Two sets:
   parahelium
   orthohelium
2. Orthohelium has fine structure
3. The energy difference between the ground state and the lowest excited state in helium is relatively large.





The potential energy of the electrons is

$$E_{\text{pot}} = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}}\right)$$



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

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

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

The Schrödinger equation is

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

with approximation

$$\mu \approx m_e = m$$

The relative distance

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

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

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

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

$$-\frac{\hbar^2}{2m}\Delta_1\psi_1(\boldsymbol{r}_1) - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_1}\psi_1(\boldsymbol{r}_1) = E_1\psi_1(\boldsymbol{r}_1)$$

$$-\frac{\hbar^2}{2m}\Delta_2\psi_2(\boldsymbol{r}_2) - \frac{e^2}{4\pi\varepsilon_0}\frac{Z}{r_2}\psi_2(\boldsymbol{r}_2) = E_2\psi_2(\boldsymbol{r}_2)$$

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:

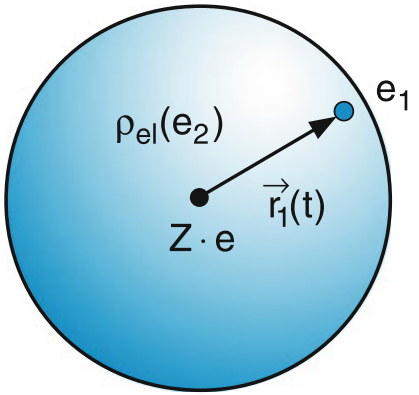
$$E_{\mathrm{He}}(1s) = -2Z^2 E_{\mathrm{H}} = -2 \cdot 4 \cdot 13.6\,\mathrm{eV}$$
$$= -108.8\,\mathrm{eV}.$$

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 He^{++}) is, however, only E_{exp}= 78.98 eV. The neglection 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

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



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

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 He^+ now has the nuclear charge +2e and the binding energy of the second electron is therefore $-Z^2E_H = -4E_H$. The total ionization energy of the He atom is then

$$E_{\mathrm{He}}(1s) = -E_{\mathrm{H}} - 4E_{\mathrm{H}} = -5E_{\mathrm{H}} = -68\,\mathrm{eV}$$

which comes much closer to the experimental value E_{He} = −78.983 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 $Z_{eff}\,e$ = +1.344e.

The coupling of electrons

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.

The coupling of electrons

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.

If the interaction energies

$$W_{l_i l_j} = a_{ij} \boldsymbol{l}_i \cdot \boldsymbol{l}_j$$

between the orbital magnetic moments of electrons e_i and e_j and

$$W_{s_i s_j} = b_{ij} \boldsymbol{s}_i \boldsymbol{s}_j$$

between their spin moments are large compared to the interaction energy

$$W_{l_i \bar{s}_i} = c_{ii} \boldsymbol{l}_i \boldsymbol{s}_i$$

The coupling of electrons

The orbital angular momenta l_i of the different electrons couple to a total orbital momentum

$$\boldsymbol{L} = \sum \boldsymbol{l}_i \quad \text{with} \quad |\boldsymbol{L}| = \sqrt{L(L+1)}\hbar$$

and the individual spins s_i to a total spin

$$\boldsymbol{S} = \sum_i \boldsymbol{s}_i \quad \text{with} \quad |\boldsymbol{S}| = \sqrt{S(S+1)}\hbar$$

of the atomic state. The total angular momentum of the electron shell is then

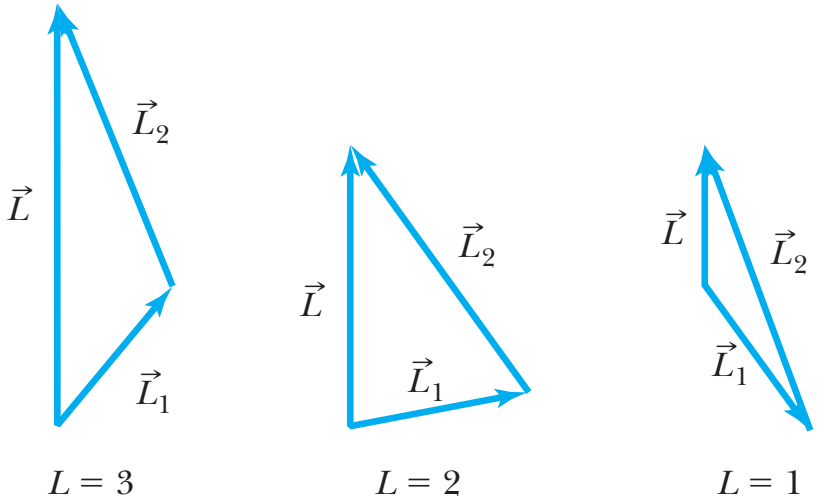
$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \quad \text{with} \quad |\boldsymbol{J}| = \sqrt{J(J+1)}\hbar.$$

The coupling of two angular momenta

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

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

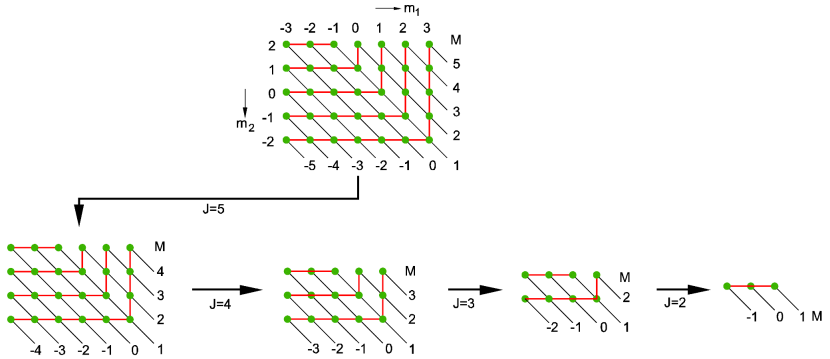
$$L = \sqrt{l(l+1)}\hbar$$



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).

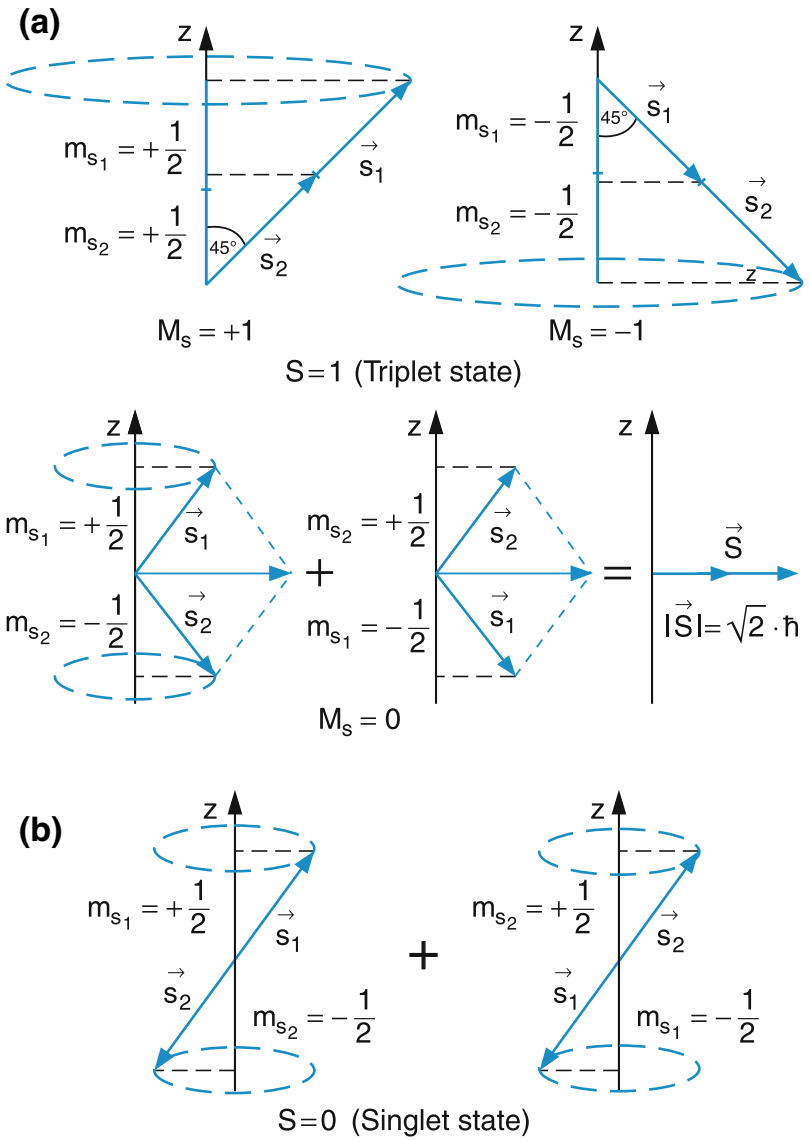
The value of 2S+1 is called the multiplicity of the state.

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



The total electron spin S has three possible projections onto the quantization axis with quantum numbers $M_s = 0, \pm 1$.

$$\chi_1^s(1,2) = \chi^+(1)\chi^+(2); \quad M_s = m_{s_1} + m_{s_2} = +1$$

$$\chi_2^s(1,2) = \chi^-(1)\chi^-(2); \quad M_s = m_{s_1} + m_{s_2} = -1$$

$$\chi_3^s(1,2) = \frac{1}{\sqrt{2}}\left[\chi^+(1)\chi^-(2) + \chi^+(2)\chi^-(1)\right] M_s = 0$$

An atomic state with total electron spin-quantum number S = 0 and therefore $M_s = 0$, which we call a singlet state

$$\chi^a = \chi^+(1)\chi^-(2) - \chi^+(2)\chi^-(1)$$

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
	1	1	4^1P_1
0 (singlet)	2	2	4^1D_2
	3	3	4^1F_3
		2	4^3P_2
1 (triplet)	1	1	4^3P_1
		0	4^3P_0
		3	4^3D_3
1 (triplet)	2	2	4^3D_2
		1	4^3D_1
		4	4^3F_4
1 (triplet)	3	3	4^3F_3
		2	4^3F_2

The fine structure

The energy of a fine structure component is

$$E_J = E(n, L, S) + C \cdot \boldsymbol{L} \cdot \boldsymbol{S},$$

The energy of a fine structure component is where the last term gives the coupling energy of the interaction between total orbital angular momentum L and total spin S. The coupling constant C is given in units of [1 $kg^{-1}\,m^{-2}$].

The energy of a fine structure component is

$$\boldsymbol{J}^2 = (\boldsymbol{L} + \boldsymbol{S})^2 = \boldsymbol{L}^2 + \boldsymbol{S}^2 + 2\boldsymbol{L} \cdot \boldsymbol{S}$$

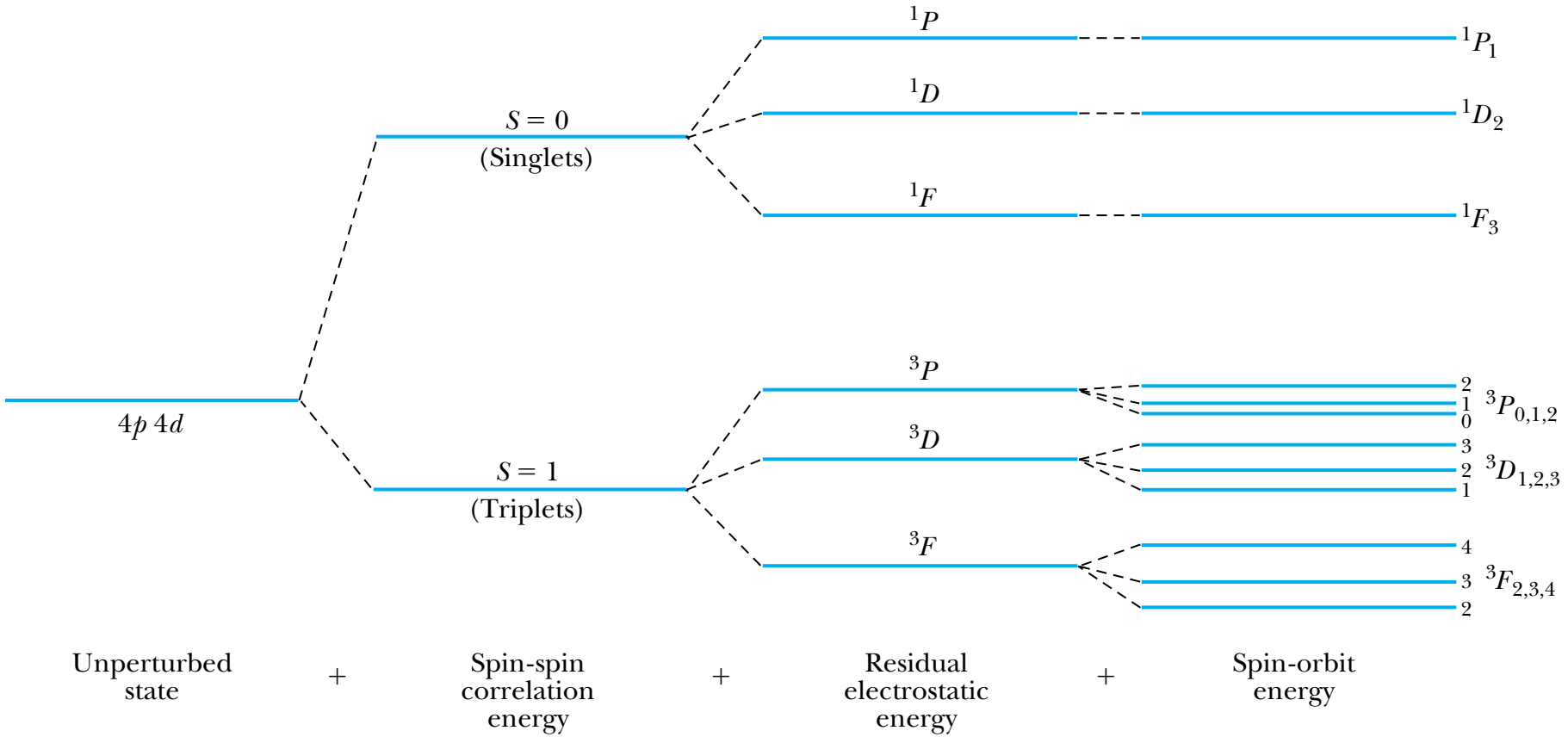
we obtain for the fine structure coupling energies

$$\boldsymbol{C} \cdot \boldsymbol{L} \cdot \boldsymbol{S}$$

$$= \frac{1}{2} C[J(J+1) - L(L+1) - S(S+1)]\hbar^2.$$

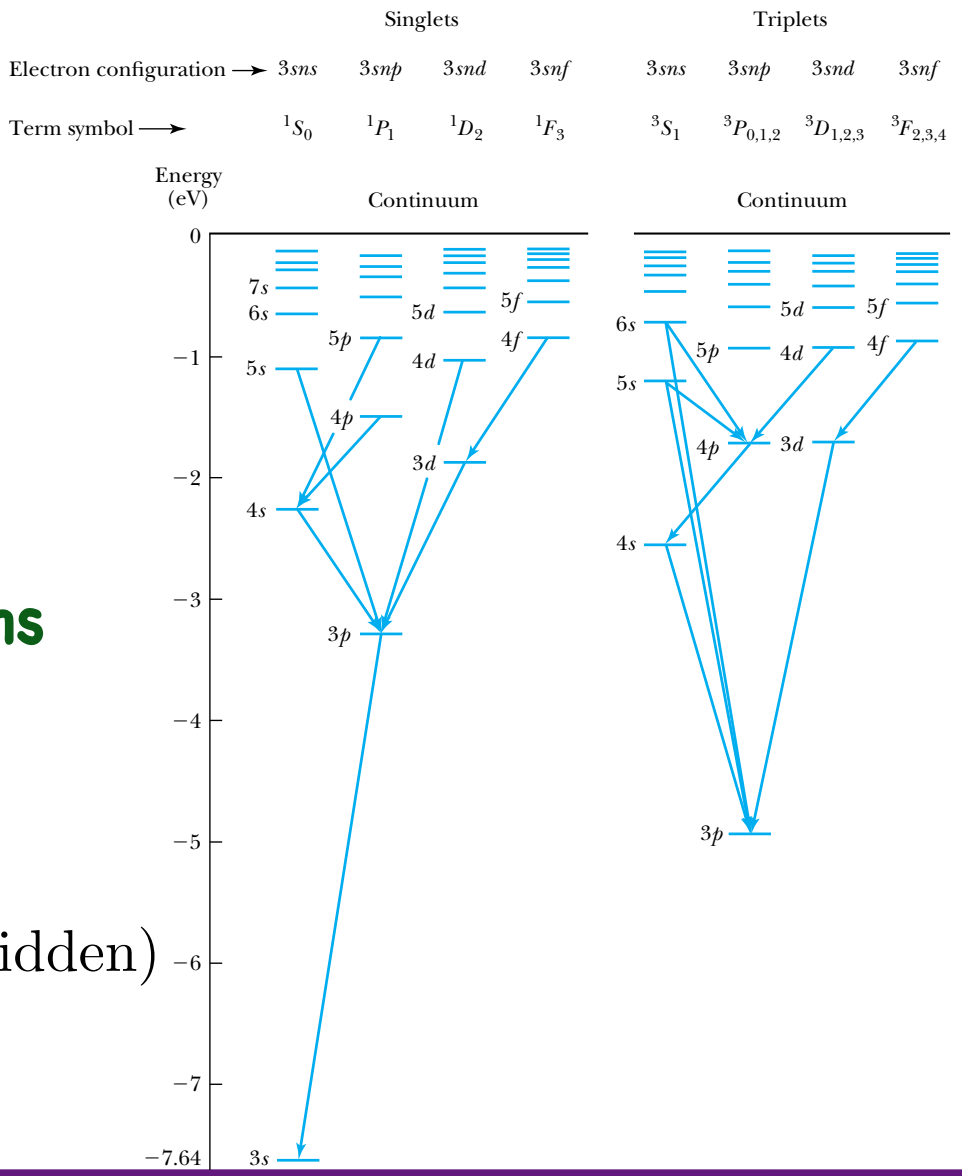
The coupling of two electrons

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

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

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

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

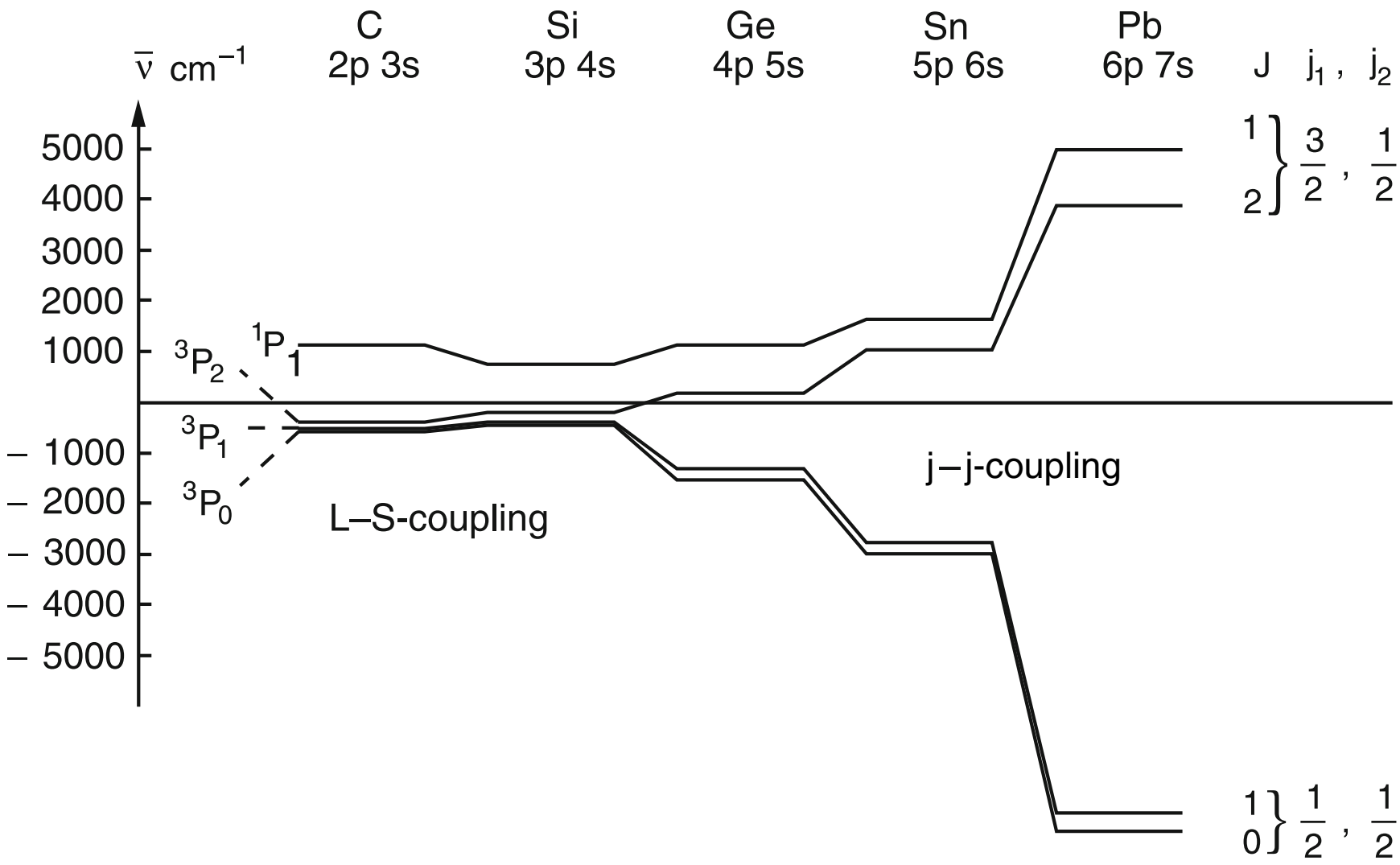
$$j_i = l_i + s_i \qquad W_{l_i s_i} = c_{ii} \boldsymbol{l}_i \boldsymbol{s}_i$$

and then

$$\boldsymbol{J} = \sum \boldsymbol{j}_i .$$

In the limiting case of j-j coupling the total orbital angular momentum L and the total spin S are no longer defined, although the individual vectors l_i and s_i are known. There are no longer S, P, D . . . levels and also no distinction between singlet, doublet or triplet levels can be made.

The coupling of two electrons



The allowed transitions

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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

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

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

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

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

A classical oscillating electric dipole

$$\boldsymbol{p} = q\boldsymbol{r} = \boldsymbol{p}_0 \sin \omega t$$

emits the average power, integrated over all directions ϑ against the dipole axis

$$\overline{P} = \frac{2}{3}\frac{\overline{p^2}\omega^4}{4\pi\varepsilon_0 c^3} \quad \text{with} \quad \overline{p^2} = \frac{1}{2}p_0^2$$

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.

Selection rules

It follows that for the spontaneously emitted radi- ation 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

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

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

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

must be different from zero.

Selection rules

The hydrogenous wave functions are

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

Tor linearly polarized light with the electric field vector E = {0, 0, E_o} only the z-component of M_{ik} contributes to the spontaneous emission. We choose the z-axis as quantization axis. With z = r cos ϑ the z-component becomes

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

$$\times \int_{\varphi=0}^{2\pi} \mathrm{e}^{\mathrm{i}(m_k-m_i)\varphi}\,\mathrm{d}\varphi.$$

Selection rules

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 σ^+-light can be written as $E^+ = E_x + iE_y$ and for σ^--light is $E^- = E_x - iE_y$.

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

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

$$x = r\sin\vartheta\,\cos\varphi \qquad y = r\sin\vartheta\,\sin\varphi$$

Selection rules

The electric dipole

$$V_{\mathrm{E1}}(t) = -\boldsymbol{d}\cdot\boldsymbol{E}(\boldsymbol{R},t)\ .$$

The magnetic dipole

$$V_{\mathrm{M1}} = -\boldsymbol{m}\cdot\boldsymbol{B}(\boldsymbol{R},t)\ ,$$

The electric quadrupole

$$V_{\mathrm{E2}}(t) = -\frac{1}{6}\sum_{i,j=1}^{3} Q_{ij}\,\frac{\partial}{\partial R_i}E_j(\boldsymbol{R},t)\ .$$

	Electric dipole (E1) (*allowed*)	Magnetic dipole (M1) (*forbidden*)	Electric quadrupole (E2) (*forbidden*)
Rigorous rules	1. $\Delta J = 0, \pm 1$ (except $0 \not\leftrightarrow 0$)	$\Delta J = 0, \pm 1$ (except $0 \not\leftrightarrow 0$)	$\Delta J = 0, \pm 1, \pm 2$ (except $0 \not\leftrightarrow 0, 1/2 \not\leftrightarrow 1/2, 0 \not\leftrightarrow 1$)
	2. $\Delta M = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1$ (except $0 \not\leftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1, \pm 2$
	3. Parity change	No parity change	No parity change
With negligible configuration interaction	4. One electron jumping, with $\Delta l = \pm 1$, Δn arbitrary	No change in electron configuration; i.e., for all electrons, $\Delta l = 0$, $\Delta n = 0$	No change in electron configuration; *or* one electron jumping with $\Delta l = 0, \pm 2$, Δn arbitrary
For LS coupling only	5. $\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
	6. $\Delta L = 0, \pm 1$ (except $0 \not\leftrightarrow 0$)	$\Delta L = 0$ $\Delta J = \pm 1$	$\Delta L = 0, \pm 1, \pm 2$ (except $0 \not\leftrightarrow 0, 0 \not\leftrightarrow 1$)

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

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

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

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

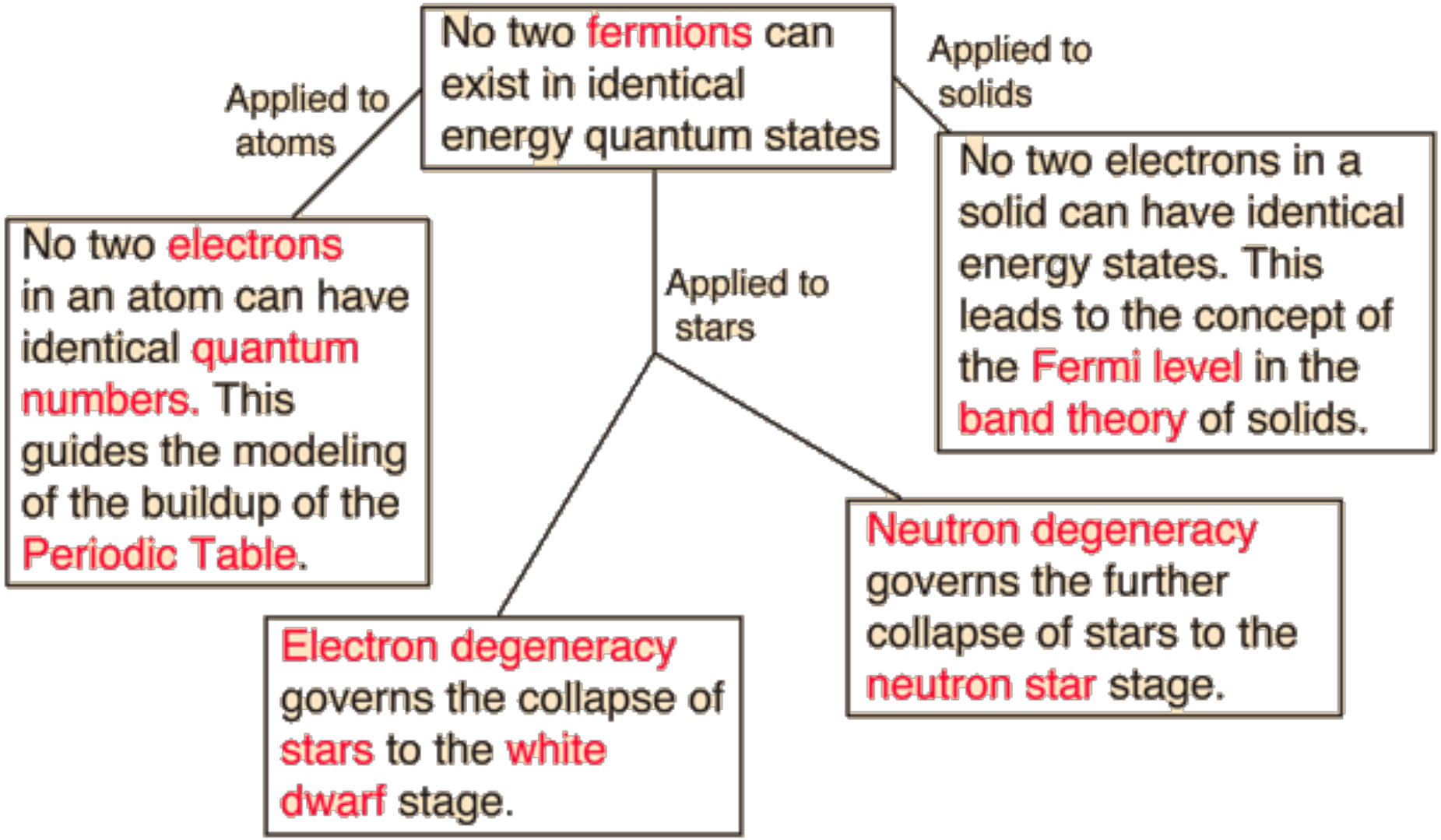
The size of atom

The atom of metal

The independent motion of nucleon

The colors of quarks

The applications



The shell and subshell

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

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.

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

The shell and subshell

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.

Shell and subshell capacities

The time-averaged total charge distribution of all $2n^2$ electrons with the same principal quantum number n

$$e|\psi_n|^2 = e\sum_l \sum_{m_l} |\psi_{n,l,m_l}|^2 = C \cdot e \sum_l |R_{n,l}(r)|^2$$

is obtained by summation over the squares of all possible wave functions with $l<n$ and $-l \le m_l \le +l$, where C is a normalization factor.

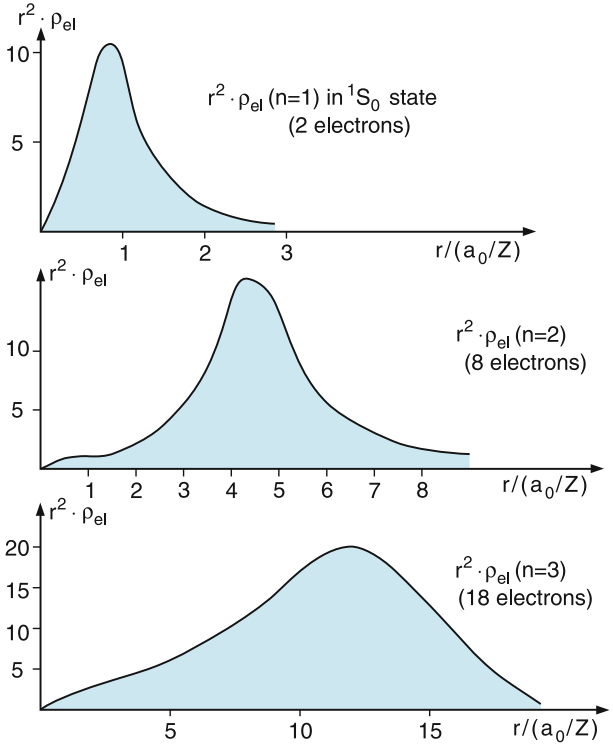
Such a spherically symmetric charge distribution is called an electron shell. The different shells are labeled as follows:

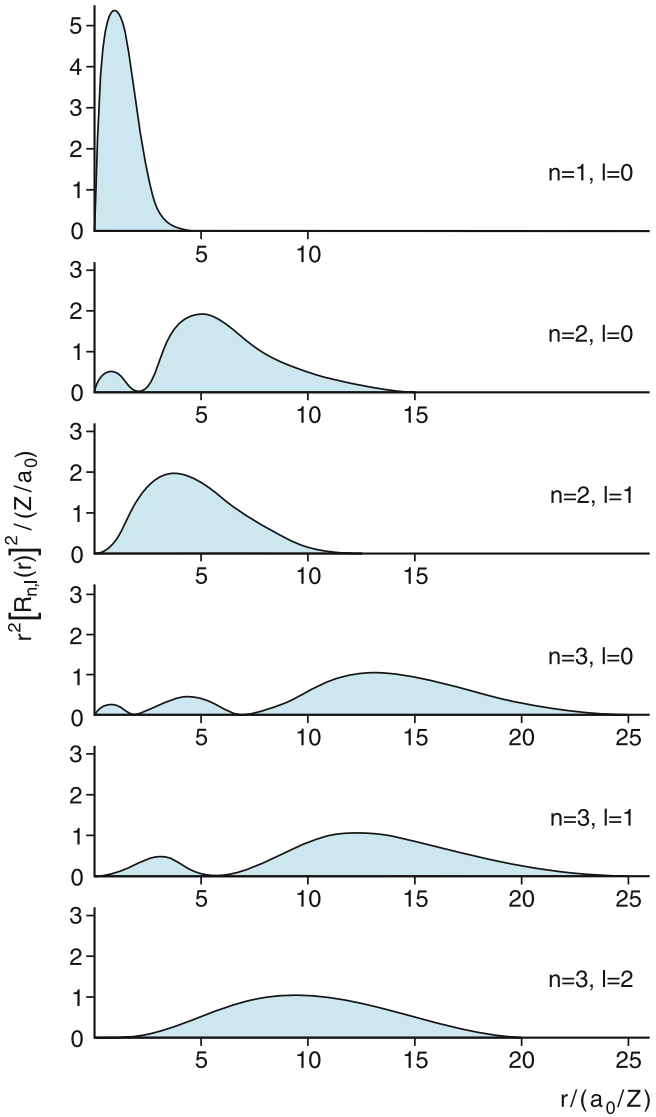
$n = 1$: K-shell, $n = 4$: N-shell

$n = 2$: L-shell, $n = 5$: O-shell

$n = 3$: M-shell, $n = 6$: P-shell

Shell and subshell capacities

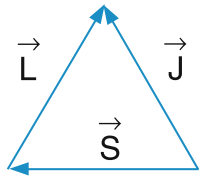




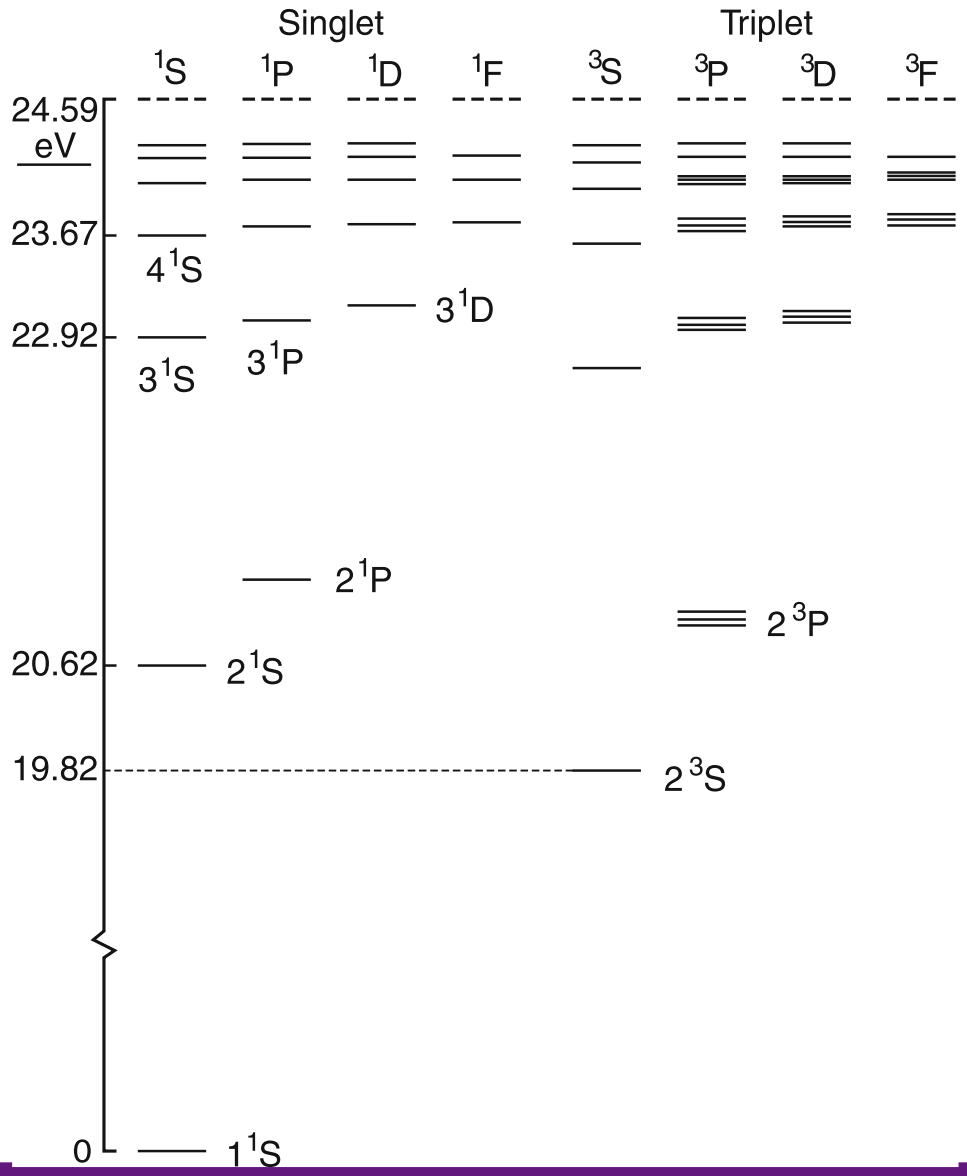
Shell	K	L	M	N	O
Maximum number of electrons in shell X	2	8	18	32	50
Subshells	$1s$	$2s\ 2p$	$3s\ 3p\ 3d$	$4s\ 4p\ 4d\ 4f$	$+5g$
Number of electrons	2	2 6	2 6 10	2 6 10 14	18
Total number of electrons up to the filled shell X	2	10	28	60	110

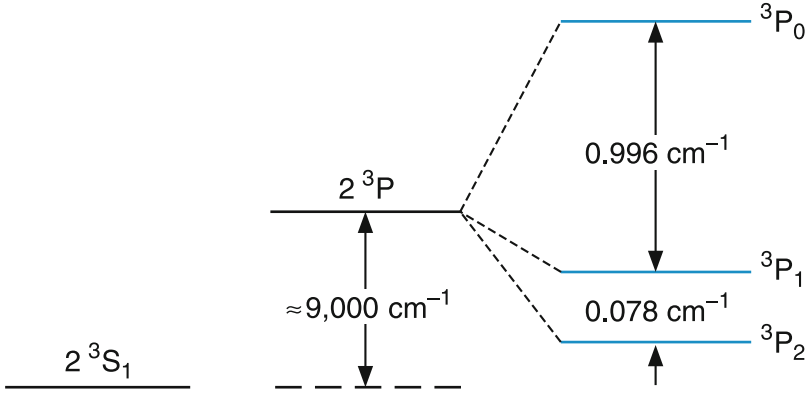
The spectra of helium

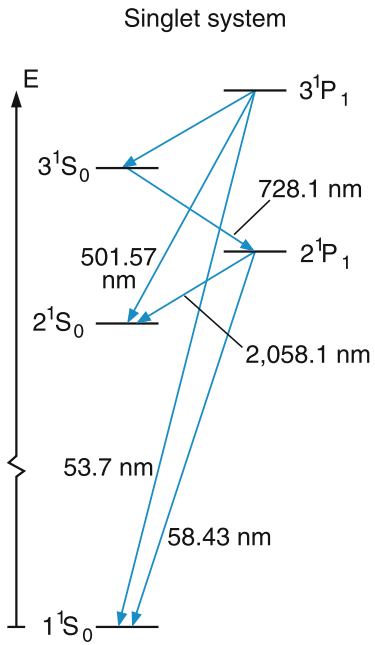
Symbolic representation of the quantum numbers n, L and S for the ground state and some excited states of the helium atom.

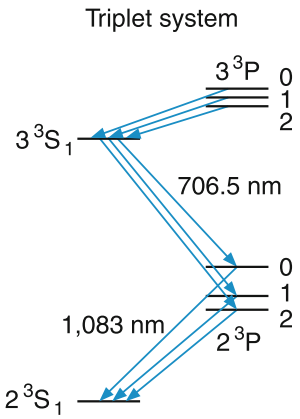
m_{l_2}	0	0	0	1	1	1
$\vec{S}(n=2)$		↓	↑	↑	↓	↑ or ↓
$\vec{S}(n=1)$	↑ ↓	↑	↑	↑	↓	↑ or ↓
Coupling of angular momentum	• •	• •	↑ •	↑ ↑	↓ ↑	
	S = 0, L = 0	S = 0, L = 0	S = 1, L = 0	S = 1, L = 1	S = 1, L = 1	S=1, L=1
Total angular momentum	J = 0	J = 0	J = 1	J = 2	J = 0	J = 1
State	1^1S_0	2^1S_0	2^3S_1	2^3P_2	2^3P_0	2^3P_1

The spectra of helium







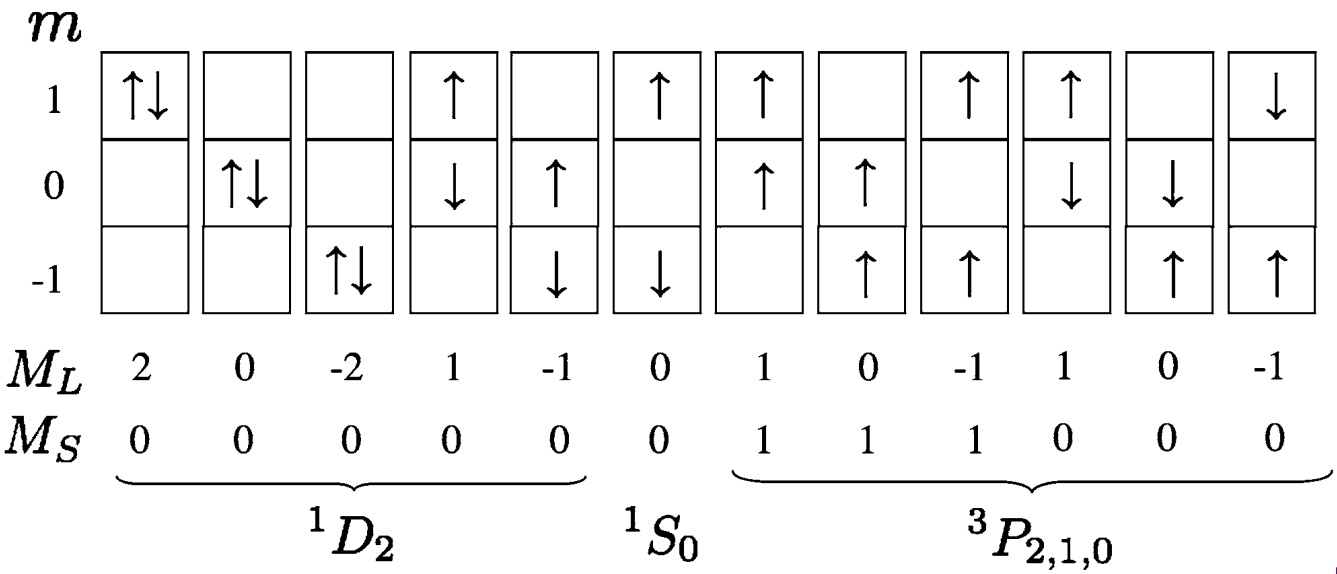


The equivalent electrons

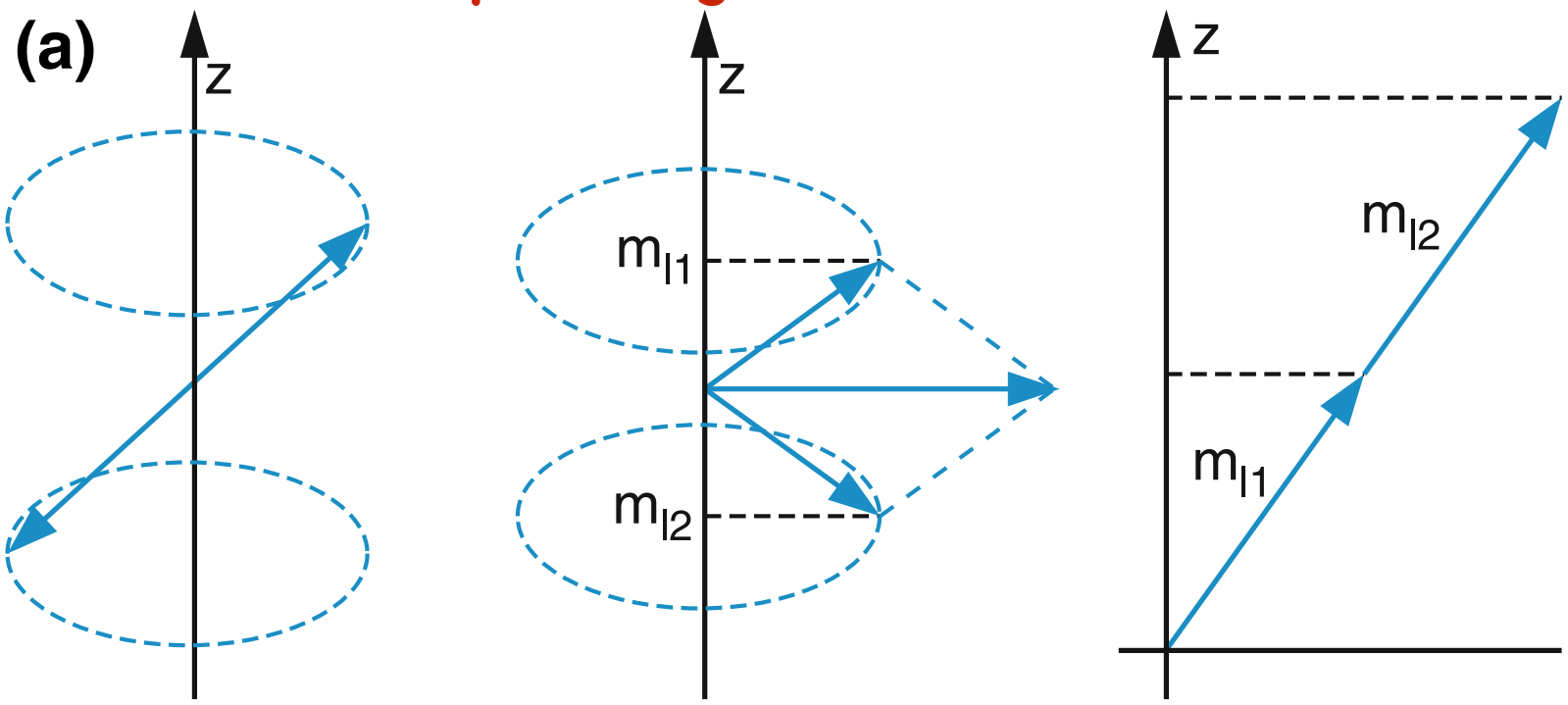
Equivalent electrons: those which belong to same (n,l) sub-shells

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



Vector model of the p^2 configuration



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

S term

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

$M=0$

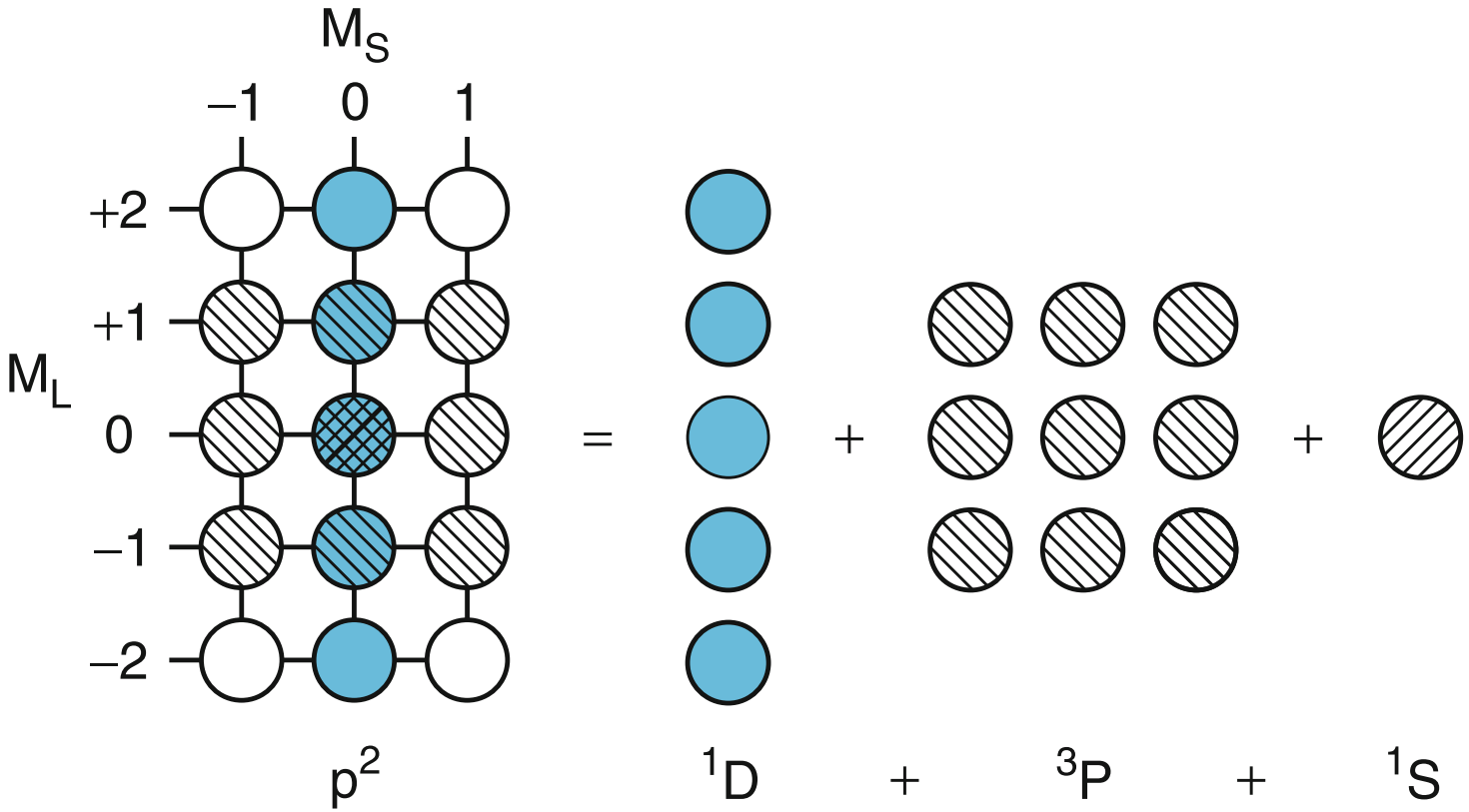
P term

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

$M=2$

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	$^3S_1$, $^1P_1$, $^3D_{1,2,3}$ } only for $n_1 \neq n_2$
	1	0	1	
	2	1	1, 2, 3	

The equivalent electrons

L	S	m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	M_S	M_J	Term
0	0	0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	$^1S_0$
1	0	0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	$^3P_0$
1	1	1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	$+1$	$+1$	$^3P_1$
		1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	0	
		1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	
1	1	1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	$+1$	$+2$	$^3P_2$
		1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	$+1$	$+1$	
		0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	
		1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	
		0	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-2	
2	0	$+1$	$+1$	$+\frac{1}{2}$	$-\frac{1}{2}$	0	$+2$	$^1D_2$
		$+1$	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	$+1$	
		1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	
		0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	-1	
		-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	-2	

The equivalent electrons

Total electron spin and multiplicity of atomic states resulting from different numbers of valence electrons

Electrons	Spin quantum number m_s	Multiplicity
1	$m_s = \frac{1}{2}$	Doublet
2	$m_{s1} = +\frac{1}{2}, m_{s2} = +\frac{1}{2} \Rightarrow S = 1$	Triplet
	$m_{s1} = +\frac{1}{2}, m_{s2} = -\frac{1}{2} \Rightarrow S = 0$	Singlet
3	$+\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2} \Rightarrow S = \frac{1}{2}$	Doublet
	$+\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2} \Rightarrow S = \frac{3}{2}$	Quartet
4	$+\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2} \Rightarrow S = 0$	Singlet
	$+\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2} \Rightarrow S = 1$	Triplet
	$+\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2} \Rightarrow S = 2$	Quintet

The equivalent electrons

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

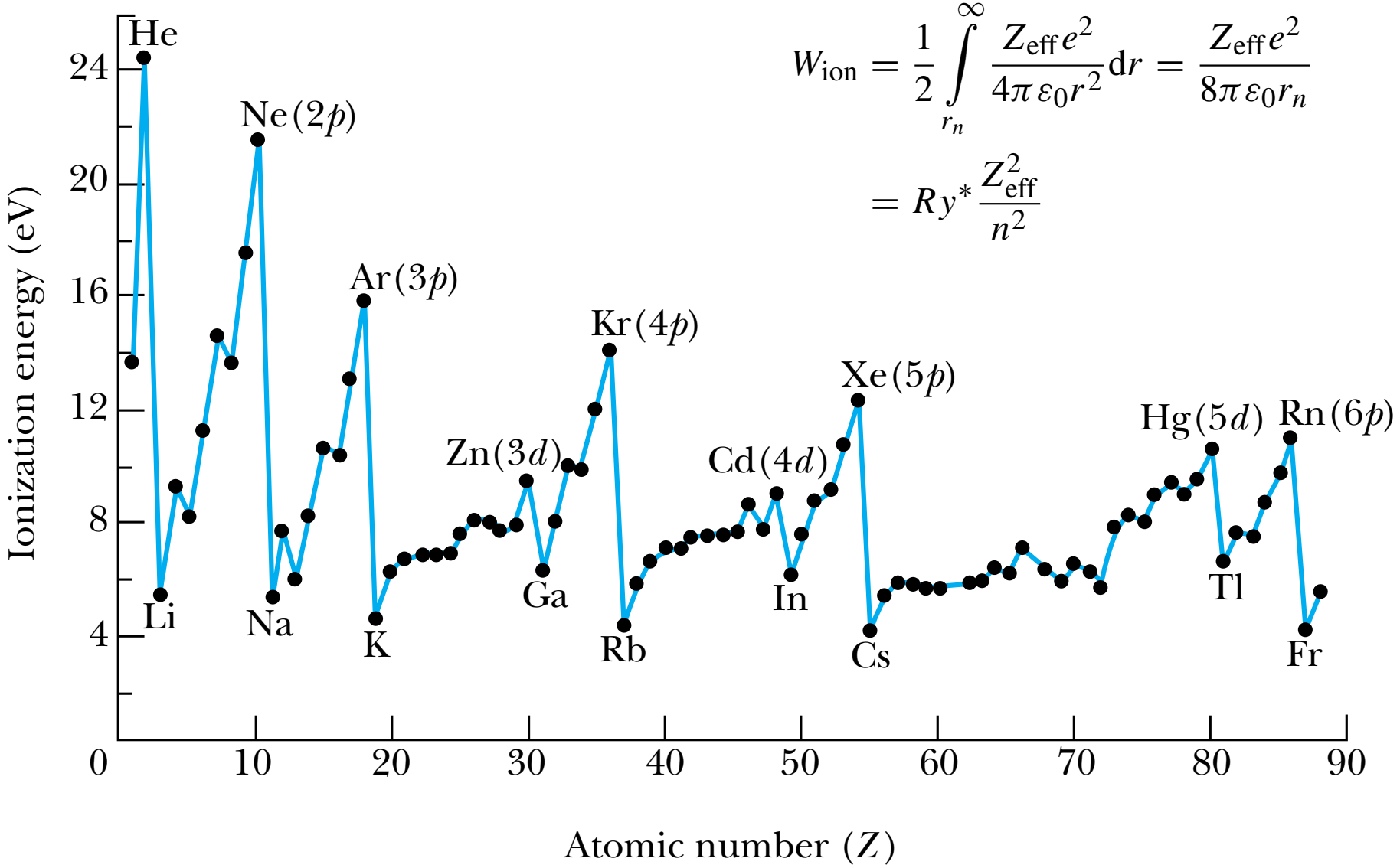
Periodic Table of Elements

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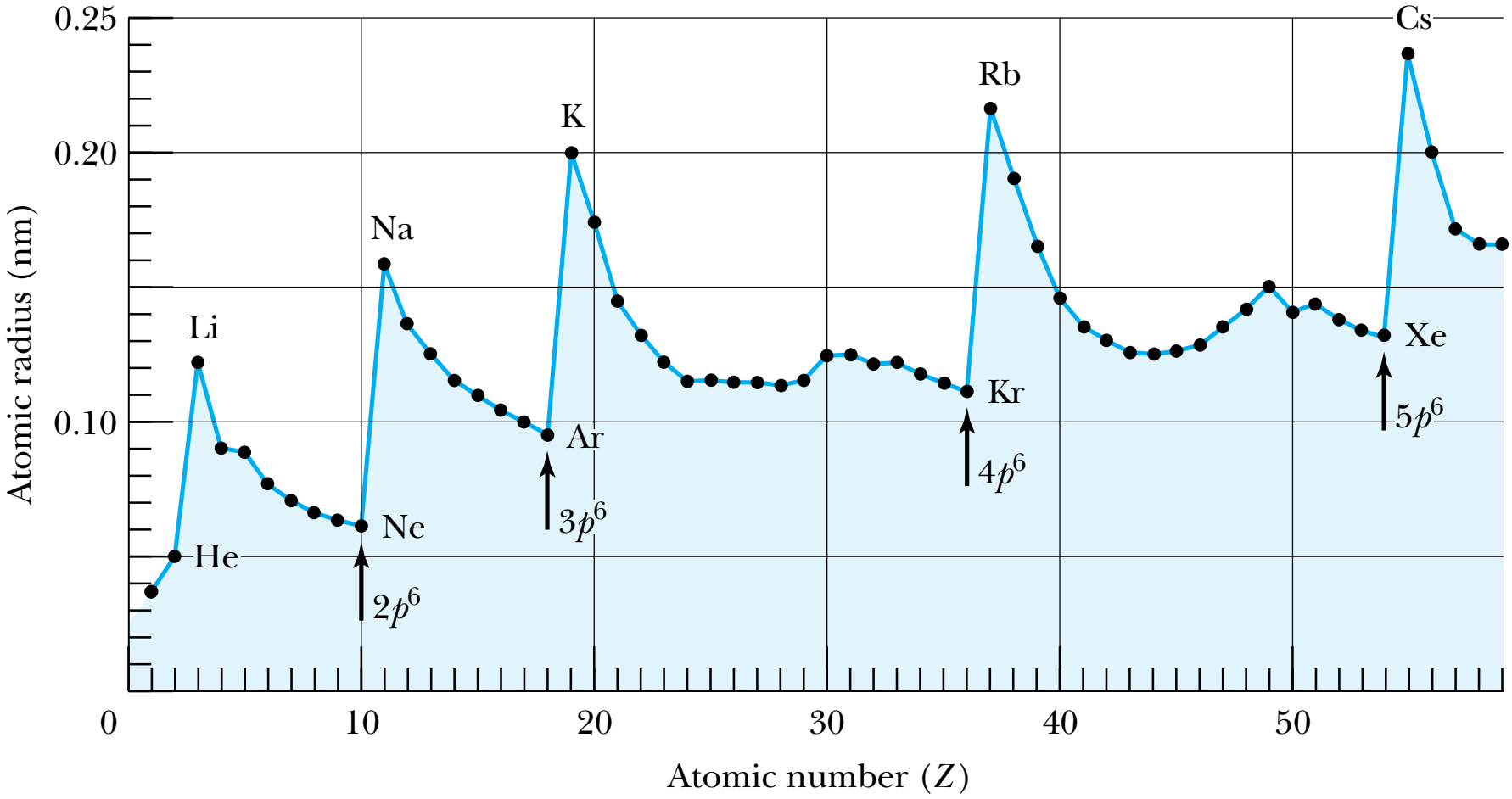
Closed shells	Groups: 1 Alkalis	2 Alkaline earths	3–12 Transition elements	13	14	15	16	17	18 Rare Halogens gases
	1 **H** $1s$								2 **He** $1s^2$
$1s^2$	3 **Li** $2s^1$	4 **Be** $2s^2$		5 **B** $2s^2\,2p^1$	6 **C** $2s^2\,2p^2$	7 **N** $2s^2\,2p^3$	8 **O** $2s^2\,2p^4$	9 **F** $2s^2\,2p^5$	10 **Ne** $2s^2\,2p^6$
$2s^2 2p^6$	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** $3s^2\,3p^6$
$3s^2 3p^6$	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** $3d^{10}\,4s^2\,4p^6$
$3d^{10}4s^2 4p^6$	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** $4d^{10}\,5s^2\,5p^6$
$4d^{10}5s^2 5p^6$	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** $4f^{14}\,5d^{10}\,6s^2\,6p^6$
$4f^{14}5d^{10}6s^2 6p^6$	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



Atomic radii



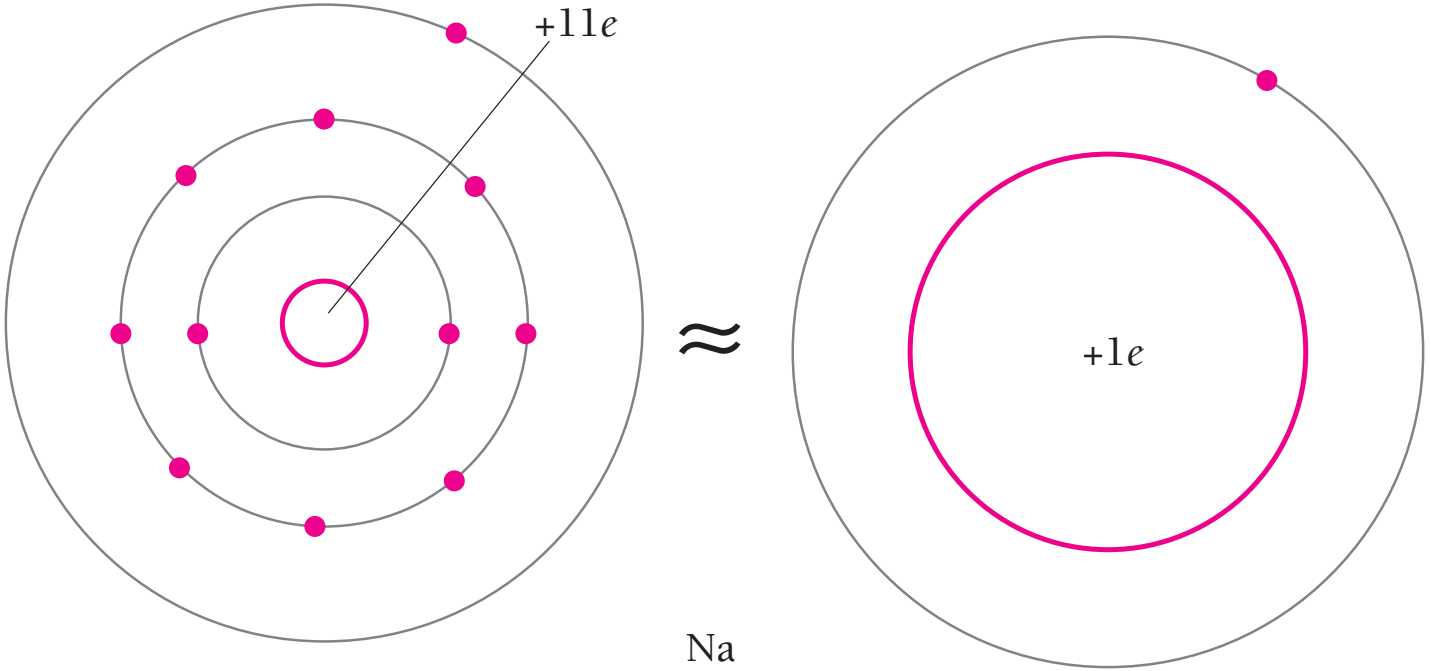
Explaining the Periodic Table

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.

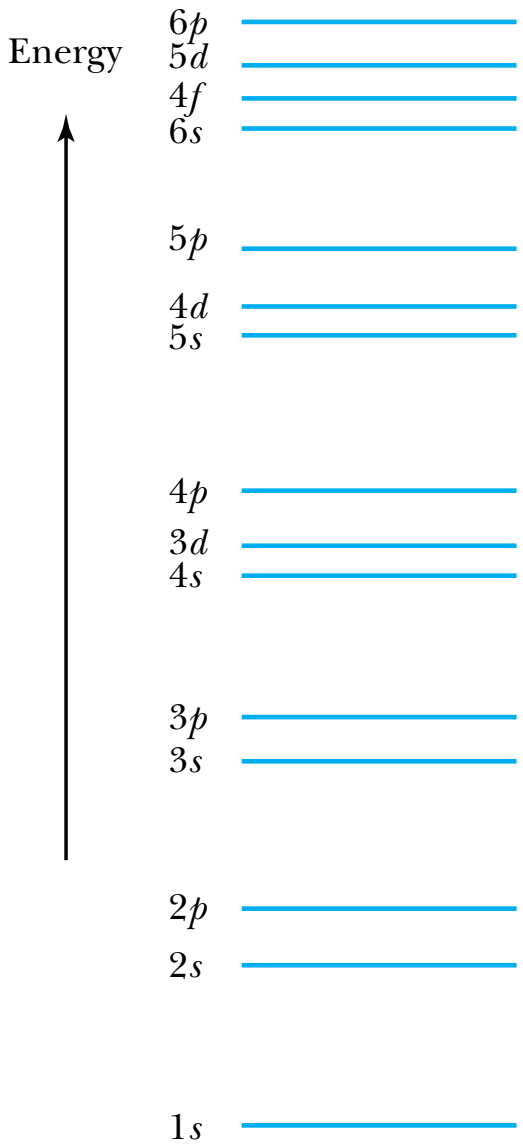
The electrons in a closed shell are all very tightly bound, since the positive nuclear charge is large relative to the negative charge of the inner shielding electrons

Explaning the Periodic Table

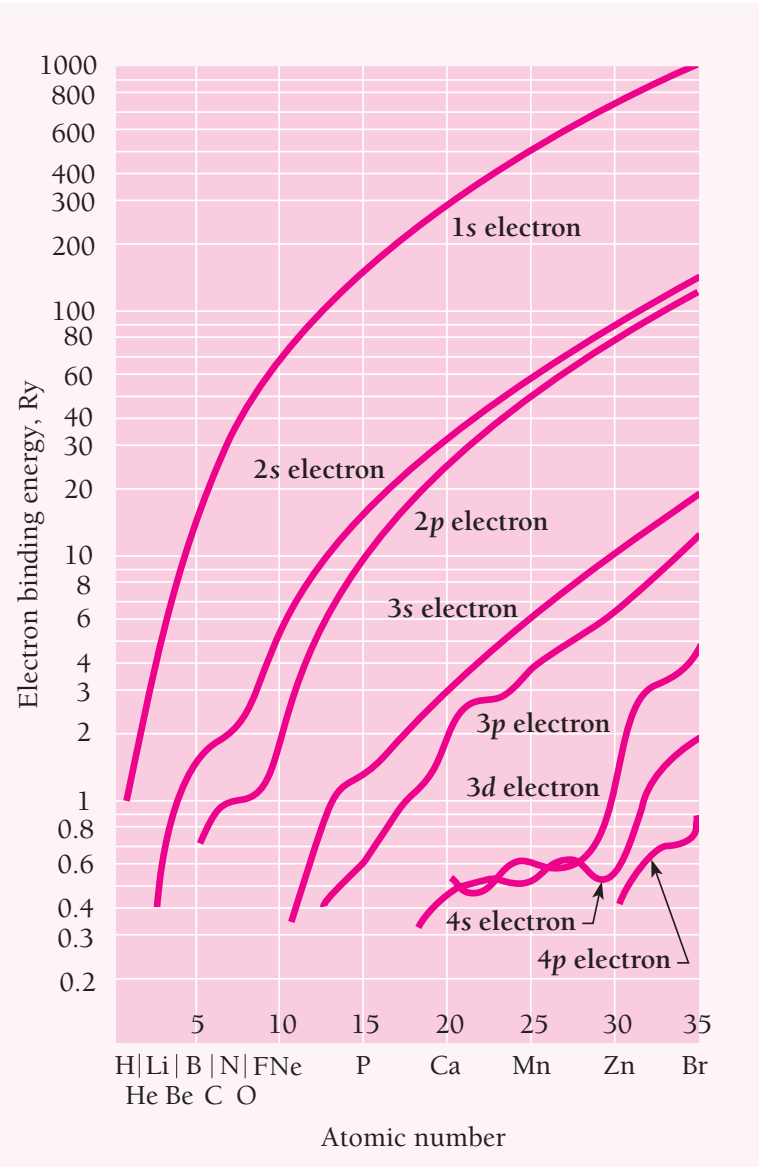


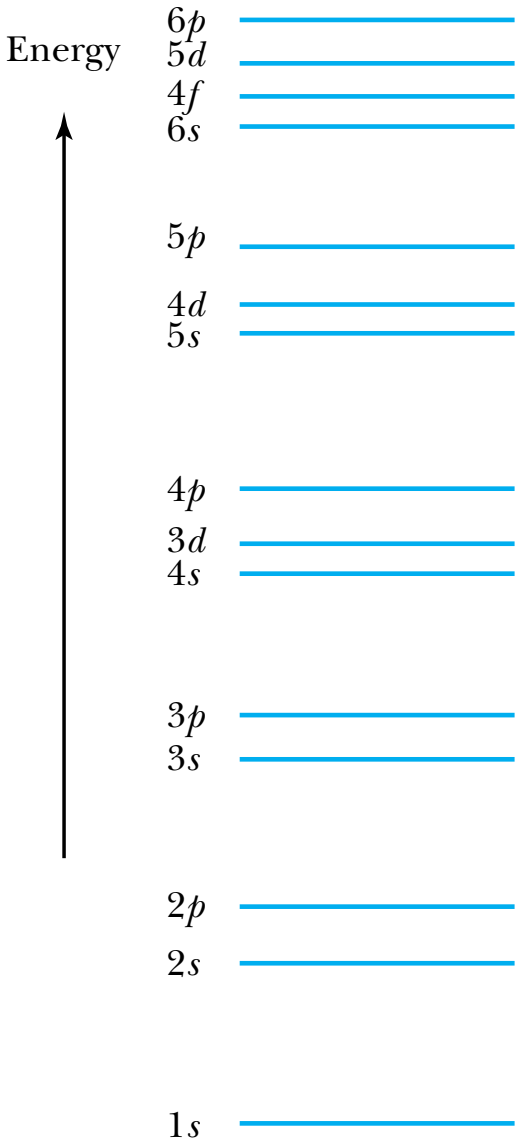
Shell and subshell capacities

n	ℓ	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

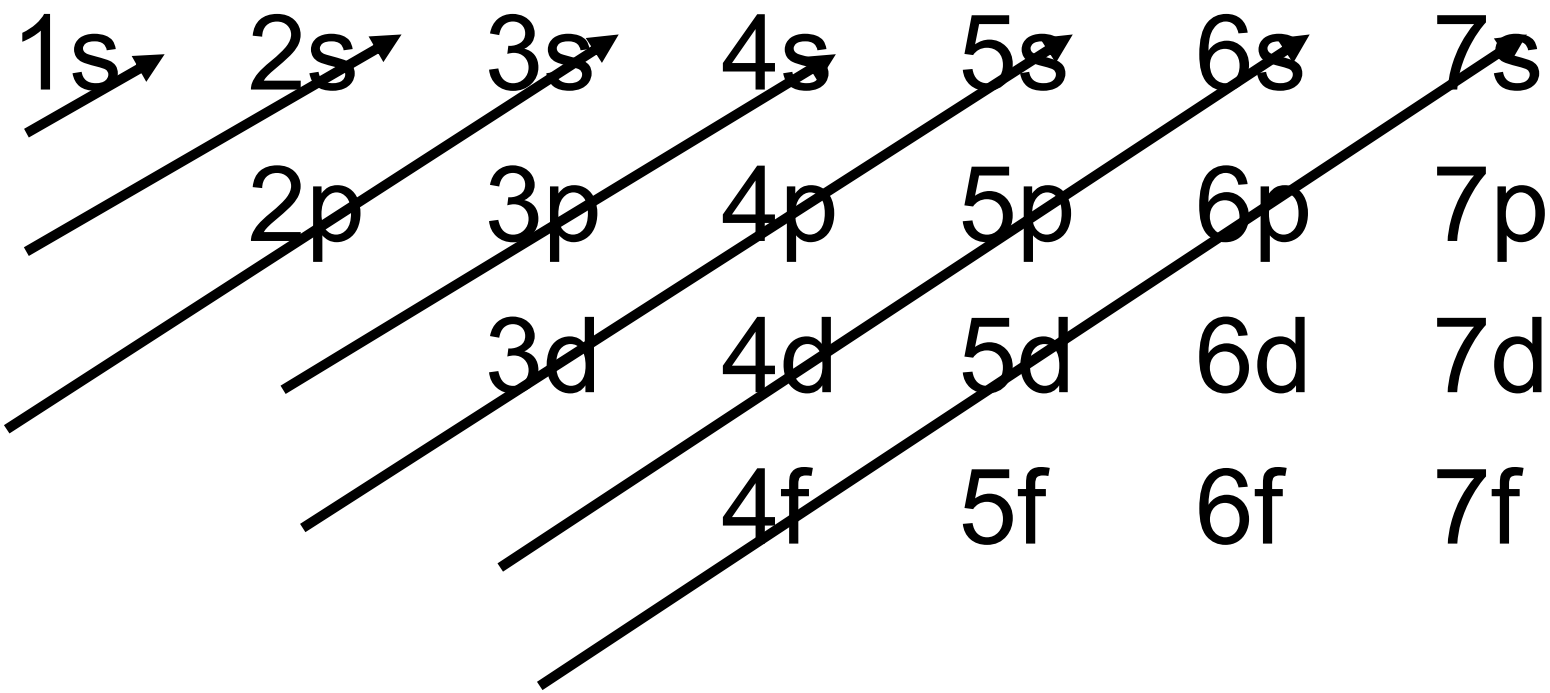


Shell and subshell capacities





The Diagonal Rule for Configurations

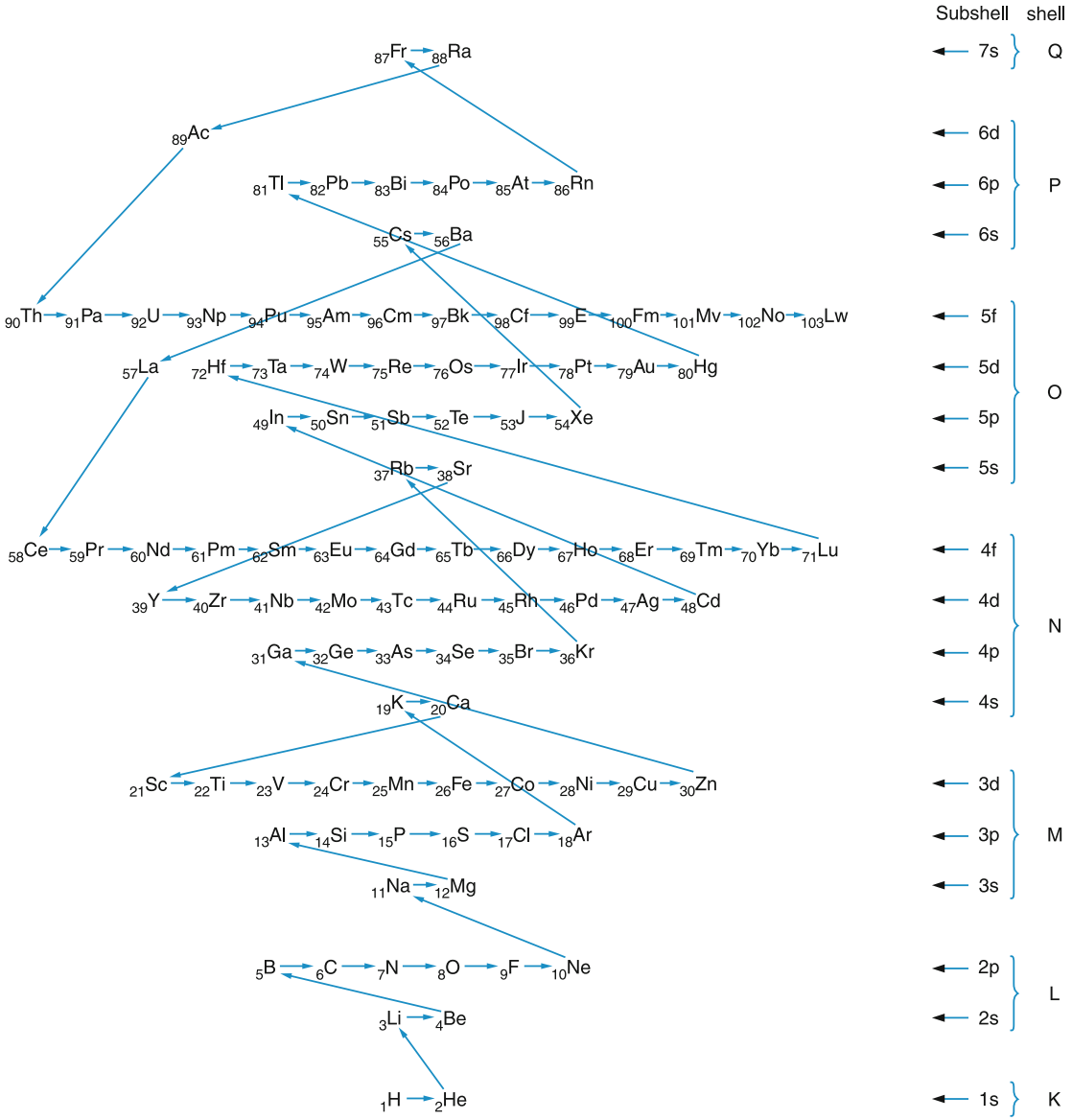


If n+l is same, fill the configuration with smaller n first

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

and n is different, fill larger n

The Diagonal Rule for Configurations



The Diagonal Rule for Configurations

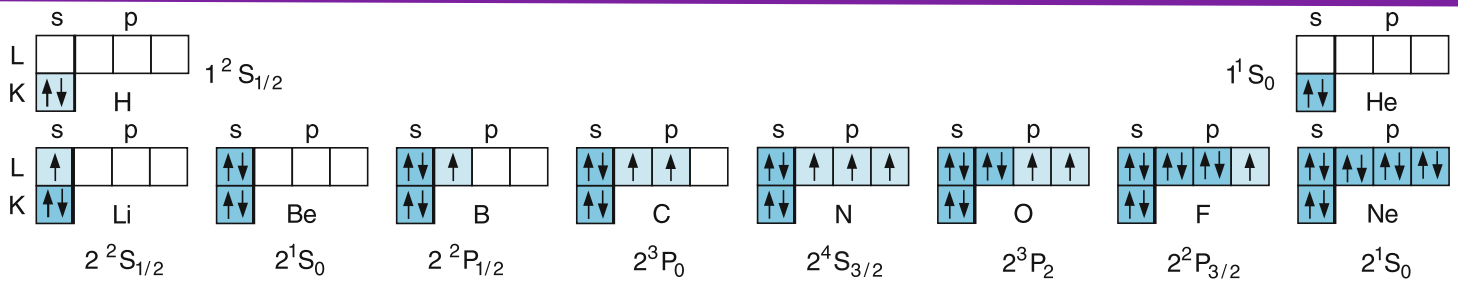
Shell			K	L		M			O	Shell			K	L		M			N			O	
Z		Element	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	Z		Element	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$5s$	$5p$
1	H	Hydrogen	1							28	Ni	Nickel	2	2	6	2	6	8	2				
2	He	Helium	2							29	Cu	Copper	2	2	6	2	6	10	1				
3	Li	Lithium	2	1						30	Zn	Zink	2	2	6	2	6	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

The ground state of atom

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	$1s^2 2s^2 2p^6$	↑↓ ↑↓ ↑↓

Al: $1s^2 2s^2 2p^6 3s^2 3p^1$ — 1*s* 2*s* 2*p* 3*s* 3*p*

Al^{3+}: $1s^2 2s^2 2p^6$ — 1*s* 2*s* 2*p*

Cr: $[Ar]4s^1 3d^5$ — [Ar] 4*s* 3*d*

Cr^{2+}: $[Ar]3d^4$ — [Ar] 4*s* 3*d*

Lande interval rule

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.

Excited Atomic States

One speaks of one-electron excitation if in the independent electron model only the quantum numbers of one electron are changed while they remain the same for all other electrons.

The smallest energy is required, when an electron in the outer valence shell is excited into higher states. The excitation energy of these valence electrons ranges from 1-10 eV.

For some states this transition probability is very small and the lifetime correspondingly long. Such states are called metastable states.

Excited Atomic States

1. Lifetimes of some excited states:

$$\mathrm{H}(2^2P_{1/2}): \quad \tau = 1.5 \times 10^{-9}\,\mathrm{s}$$
$$\mathrm{He}(2^1P_1): \quad \tau = 0.5 \times 10^{-9}\,\mathrm{s}$$
$$\mathrm{Na}(3^2P_{1/2}): \quad \tau = 16 \times 10^{-9}\,\mathrm{s}$$

2. Lifetimes of metastable states:

$$\mathrm{H}(2^2S_{1/2}): \quad \tau = 8\,\mathrm{s}$$
$$\mathrm{He}(2^1S_0): \quad \tau = 19.6\,\mathrm{ms}$$
$$\mathrm{He}(2^3S_1): \quad \tau = 7870s$$

Under special conditions two electrons can be excited simultaneously. Assume, for instance, that two electrons from the 2s state of Be are excited into higher states.

Excited Atomic States

The two excited electrons can populate the 2p state, or one electron is excited into the 2p state and the other into the 3p state, etc. The total excitation energy is then

$$E = E_1 + E_2 + \Delta E,$$

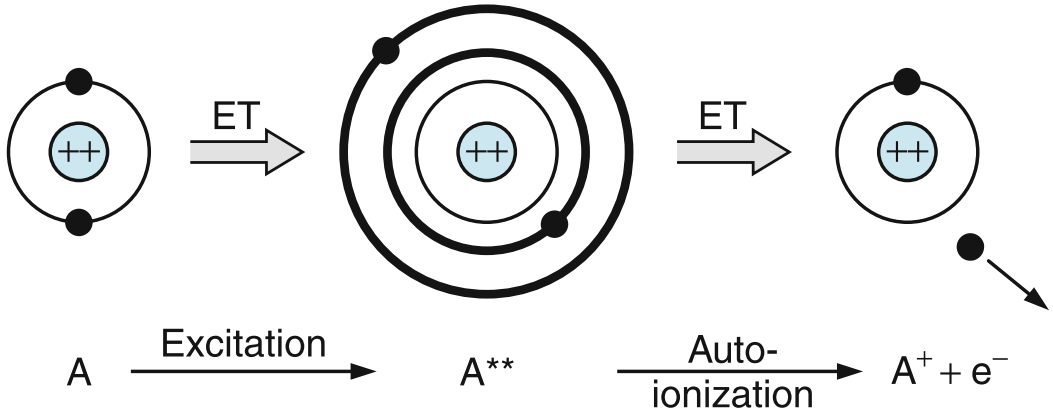
where E_i is the excitation energy for the single excitation of electron e_i and $\mathscr{D}E$ is the change in the interaction energy between the two electrons and with the core, caused by the excitation of the two electrons.

The doubly excited atomic state can decay either by emission of two photons, or the energy of one excited electron can be transferred to the other excited electron, due to the Coulomb interaction between the two electrons.

Excited Atomic States

Since the total energy must be conserved, this process of energy transfer from one electron to the other is only possible, if an excited atomic state exists, that matches the energy E^* of this highly excited electron.

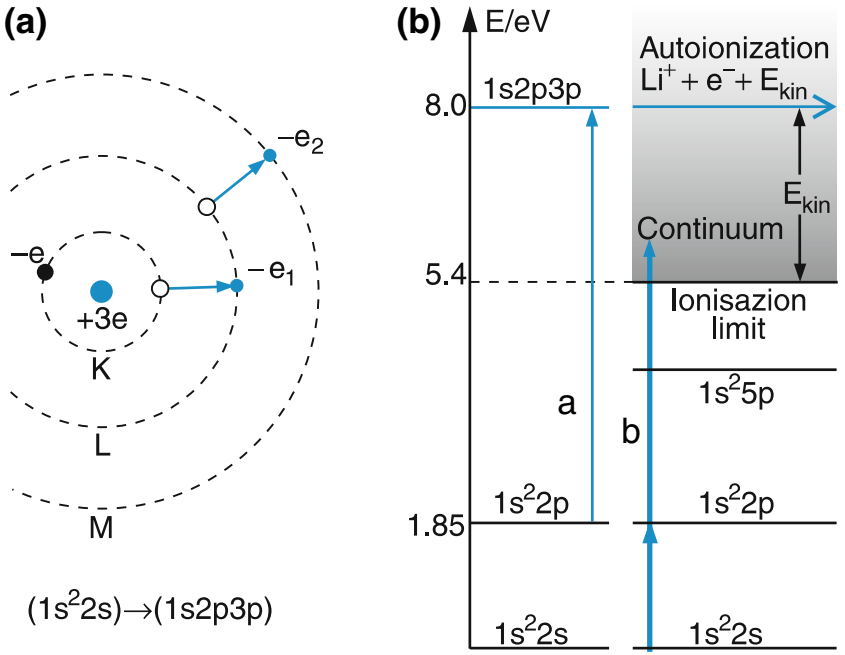
For the continuous energy spectrum $E^* > E_{ion}$, the transfer of the excitation energy of one of the two excited electrons to the other allows this electron to leave the atom and the atom becomes ionized



Excited Atomic States

This process is called autoionization. For the case of the doubly excited Li atom. One electron is excited from the 2s into the 2p level, the other from the 1s into the 3p level. The total energy of the doubly excited state 1s2p3p lies above the ionization energy of singly excited states at about 5.4eV.

$$E_{\text{ion}} = \lim_{n\to\infty}(1s^2np)$$



If the 2p electron transfers its energy to the 3p electron, the energy of the latter becomes higher than E_{ion} and the electron can leave the atom.

The autoionization can proceeds in two different ways:

(a) Excitation of a level above the ionization level starting from the $1s^2 2s$ ground state with subsequent transfer into the ionization continum

(b) Direct excitation into the ionization continum generally in two steps (e.g. $1s^2 2s \rightarrow 1s^2 2p \rightarrow$ ionization).

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The Physics of Atoms and Quanta

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

Exercise class

1. What are the possible energy states for atomic Oxygen?

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1. What are the possible energy states for atomic carbon?

Solution: The element carbon has two 2p subshell electrons outside the closed $2s^2$ subshell. Both electrons have l=1, so we have L=0, 1, or 2 using the LS coupling scheme. The spin angular momentum is S=0 or 1.

S	L	J	Spectroscopic Notation	
0	0	0	$^1S_0$	
	1	1	$^1P_1$	Not allowed
	2	2	$^1D_2$	
1	0	1	$^3S_1$	Not allowed
	1	0, 1, 2	$^3P_{0,1,2}$	
	2	1, 2, 3	$^3D_{1,2,3}$	Not allowed

2. The 3s state of Na has an energy of -5.14 eV. Determine the effective nuclear charge.

2. The 3s state of Na has an energy of -5.14 eV. Determine the effective nuclear charge.

Solution:

$$Z_{eff}^2 13.6/9 = 5.14, \quad Z_{eff} = 1.84e$$

3. Consider a $^2D_{5/2}$ state. (a) What are the possible values of S, L, J, and J_z? (b) What is the minimum angle between J and the z axis?

3. Consider a $^2D_{3/2}$ state. (a) What are the possible values of S, L, J, and J_z? (b) What is the minimum angle between J and the z axis?

Solution:

$$S = 1/2, L = 2, J = 3/2, J_z = -3/2,\ -1/2,\ 1/2,\ 3/2$$

$$\cos\theta = \sqrt{3/5},\ \theta = 39.23^\circ$$

4. What are the L, S, and J values for the first few excited states of helium?

4. What are the L, S, and J values for the first few excited states of helium?

Solution:

The possibilities are

$1s^1 2s^1$ $\quad L = 0$

If $S = 0$, then $J = 0$

If $S = 1$, then $J = 1$

with $S = 1$ being lowest in energy. The lowest excited state is $^3S_1$ and then comes $^1S_0$.

$1s^1 2p^1$ $\quad L = 1$

If $S = 0$, then $J = 1$

If $S = 1$, then $J = 0, 1, 2$

The state $^3P_0$ has the lowest energy of these states, followed by $^3P_1$, $^3P_2$, and $^1P_1$. The energy-level diagram for helium is shown in Figure 8.13.

5. Which electronic configuration has a lower energy: $[Ar]3d^4 4s^2$ or $[Ar]3d^5 4s^1$? Identify this element and discuss Hund's rule in this case. (Note: The notation [Ar] represents the filled configuration for Ar.)