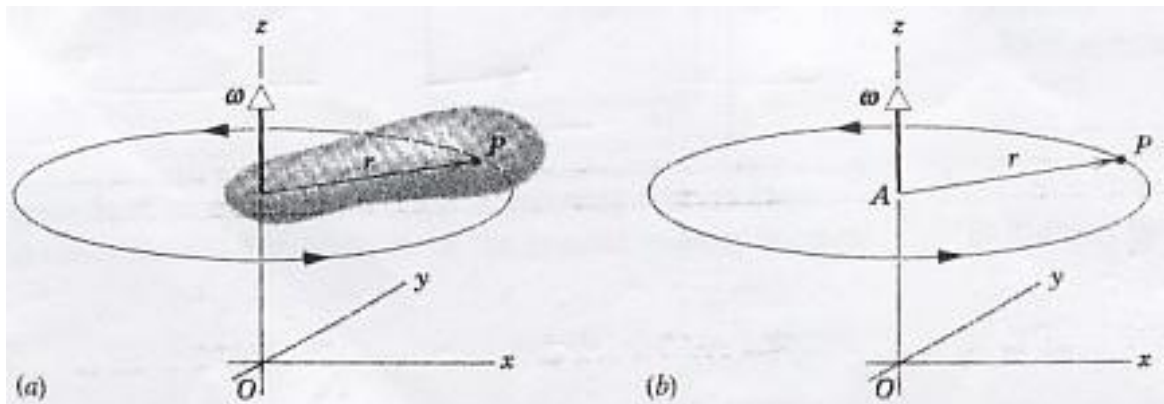


# Angular momentum

- Has a very prominent role in the atomic structure and spectroscopy.

# Recall angular momentum - in classical physics

- Rotational motion around an axis – characterized by angular position  $\Theta = s/r$  where  $s$  is the length of the arc  $r$  is the radius of rotation.
- Angular displacement  $\Delta\Theta = \Theta_2 - \Theta_1$
- Average angular velocity:  $\langle\omega\rangle = \Delta\Theta/\Delta t$ .
- Instantaneous angular velocity:  $\omega = d\Theta/dt$ .
- Angular acceleration:  $\alpha = d\omega/dt$ .
- Angular velocity and acceleration described by a vector in the direction of the axis of rotation



# Connection to linear variables

- Position:  $s = \Theta r$ .
- The derivative:  $ds/dt = (d\Theta/dt) \cdot r$ ;  $v = \omega r$ .
- Tangential acceleration:  $dv/dt = (d\omega/dt) \cdot r$ ;

$$a_t = \alpha r .$$

$$\text{Radial acceleration: } a_r = v^2/r = \omega^2 r.$$

$$\text{Kinetic energy: } K = \sum \frac{1}{2} m v^2 = \frac{1}{2} (\sum m r^2) \omega^2$$

$$\text{Moment of inertia: } I = \sum m r^2$$

Only tangential force can cause rotation:

The affect of such force depends also on point of application – Torque  $\tau = r F \sin \Phi$ .

## Newton's second law for rotation:

- $F_t = ma_t$  We had:  $\tau = F_t r = ma_t r$
- But ,  $a_t = \alpha r$  – we can write the torque as:
- $\tau = (mr^2) \alpha = I\alpha$ .

- Vectorial definition of torque:  $\tau = r \times F$  –  
Parallel to the axis of rotation.

Angular momentum:  $l = r \times p$

- In a similar way to:  $\Sigma F = dp/dt$ , we have  
 $\Sigma \tau = dl/dt$ .

As  $p = mv$  we have  $l = lw$

# Conservation of angular momentum

- Change of angular momentum by torque:

$$\Sigma \tau = dl/dt.$$

Without external torques – angular momentum is conserved.

This does not mean that the angular velocity is conserved:  $I_i \omega_i = I_f \omega_f$

Actually in atoms or molecules the angular momentum is quantized.

# Conservation in atoms

- Without external torques, total angular momentum ( $J$ ) is conserved.
- $J$  determines the magnetic dipole moment of an atom.
- Photons carry angular momentum themselves. The total angular momentum (Atom +photon) is then conserved.
- The change in  $J$  – governed by selection rules.
- External magnetic fields – creates different states of whose component along  $J$  is different

# Types of angular momentum:

- Orbital angular momentum: Result of the electron orbiting around the nucleus:
- The angular momentum is specified by two quantum numbers:  $l$  and  $m$ .
- *The magnitude of  $l$ :*

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

*and the z-component:*

$$l_z = m\hbar$$

*$l$  takes positive integer, including 0. and  $m$  from  $-l$  to  $l$ .*

*$M$  states split under electric and magnetic fields,.*

# Radial forces can not change the angular momentum:

- $\hat{r}$  is a unit vector parallel to  $r$ :

and: 
$$\frac{d\mathbf{l}}{dt} = \mathbf{\Gamma} = \mathbf{r} \times \mathbf{F} = \mathbf{r} \times F\hat{r} = 0$$

In hydrogen atoms, the force is completely radial and  $l$  is conserved.

In multi electron atoms: as long as the central field approximation is valid,  $l$  is also conserved.



# Spin angular momentum:

- Experimental observations – optical chemical and magnetic indicates the presence of spin angular momentum.
- One can see it as if the electron is spinning around its own internal axis.
- This classical analogy is incorrect. The spin is a pure quantum effect.
- Detection of spin through the Stern Gerlach experiment.

# The Stern Gerlach experiment:

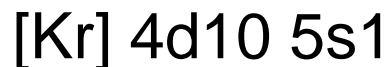
- Deflection of atomic (silver) beam by a non uniform magnetic field.

- The force on a magnetic dipole is:

$$F_z = \mu_z \frac{dB}{dz}$$

The magnetic dipole is directly proportional to the angular momentum.

- The ground state configuration of silver:



- The ground state of silver should have no angular momentum. No deflection should be observed.

# Both up and down deflection are observed.

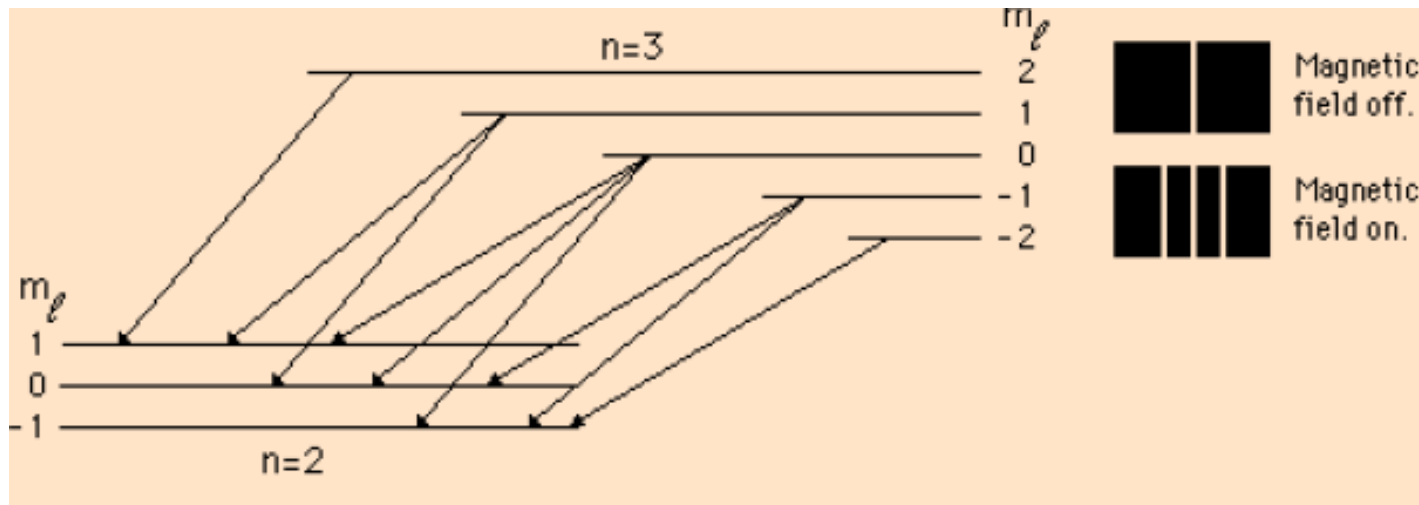
- The magnetic dipole is due to non orbital angular momentum.
- Spin angular momentum described in a similar way to the orbital angular momentum:
- The magnitude:  $|s| = \sqrt{s(s+1)}\hbar$ .
- The z – component:  $s_z = m_s\hbar$
- In a single valence shell electron:  
 $s = 1/2$ , In agreement with the  
 $m_s = \pm 1/2$ . Stern Gerlach experiment.

# Other proofs:

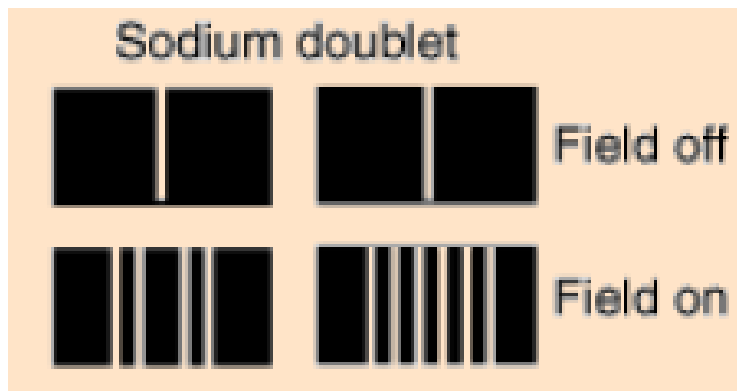
- Periodic table can not be explained without the spin.
- High resolution atomic spectroscopy gives close multiplets due to spin orbit coupling –can not be explained without the spin.
- The most direct proof – The Zeeman and the anomalous Zeeman effects:

# Splitting by a magnetic field:

- More lines than expected: The Zeeman effect for Hydrogen:

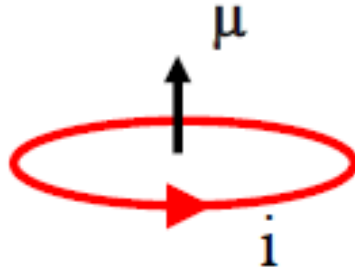


- In Sodium doublet – more lines due to the spin:



# The gyromagnetic ratio:

- Classical magnetic dipole defined by:
- $\mu = iA$



For a rotating electron we observe classically:

$$\mu = IA = \frac{qv}{2\pi r} \times \pi r^2 = \frac{q}{2m} \times mvr = \frac{q}{2m} L.$$

For a single electron: the orbital gyromagnetic ratio is  $q/2m$  and the expected moment is

$$\mu_{\text{orbital}} = -\frac{e}{2m} \vec{L} \quad \text{giving energy shifts of form} \quad \frac{eh}{2m} m_l B = \mu_B m_l B$$

# The actual picture is different:

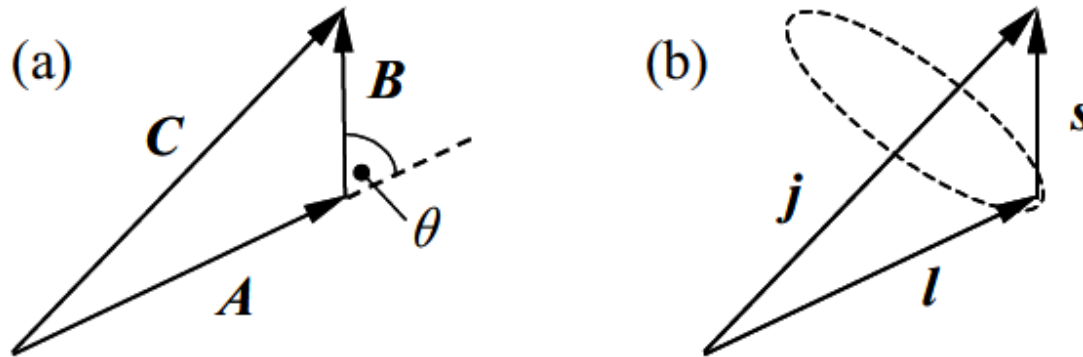
- The gyromagnetic ratio  $\gamma$  is actually twice as large:

$$|\gamma_e| = \frac{|-e|}{2m_e} g_e = g_e \mu_B / \hbar,$$

- Where  $\mu_B$  is the Bohr magneton and the  $g_e$  is dimensionless (Lande – in atoms) g factor.
- the g factor is close to 2 - in case of spin only angular momentum instead of 1 – in case of pure orbital angular momentum.

# Addition of angular momentum:

- The spin and orbital angular momentum can be added:



In classical terms  $C$  can get any value from  $(|A| + |B|)$  to  $(|A| - |B|)$ .

- In quantum terms it is  $|A| = \sqrt{A(A+1)}\hbar$
- more complicated.  $|B| = \sqrt{B(B+1)}\hbar$
- The lengths are fixed:  $|C| = \sqrt{C(C+1)}\hbar$



Also the components in the z direction are quantized.

- Therefore the rules for the allowed values of C are:

$$C = A \oplus B = (A + B), (A + B - 1), \dots, |A - B|$$

- The symbol  $\oplus$  indicates that we are adding together angular momentum quantum numbers.

# Examples:

- Different additions:

$$J = L + S, L = 3, S = 1:$$

$$J = 3 \oplus 1, 3 + 1 = 4, |3 - 1| = 2, \text{ therefore } J = 4, 3, 2.$$

$$L = l_1 + l_2, l_1 = 2, l_2 = 0:$$

$$L = 2 \oplus 0, 2 + 0 = 2, |2 - 0| = 2, \text{ therefore } L = 2.$$

$$S = s_1 + s_2, s_1 = 1/2, s_2 = 1/2:$$

$$S = 1/2 \oplus 1/2, 1/2 + 1/2 = 1, |1/2 - 1/2| = 0, \text{ therefore } S = 1, 0.$$

$$J = j_1 + j_2, j_1 = 5/2, j_2 = 3/2:$$

$$J = 5/2 \oplus 3/2, 5/2 + 3/2 = 4, |5/2 - 3/2| = 1, \text{ therefore } J = 4, 3, 2, 1.$$

# Spin orbit couplings:

- Magnetic dipoles interact with each other.
- A more detailed explanation will be given.
- Interaction between the spin magnetic dipole and the field induced by the orbit:

$$\hat{H} = -\mu_{\text{spin}} \cdot B_{\text{orbital}} \propto l \cdot s$$

- **Recall:**  $\mu_{\text{spin}} \propto s$  and  $B_{\text{orbital}} \propto l$ .
- SO coupling scales with  $Z^2$ . – significant at heavy atoms.

# Angular momentum coupling in single electron atoms

- The SO coupling is coupling the two momenta together to create a sum:

$$j = l + s.$$

- Usual rules for quantum mechanical angular momenta:

$$|j| = \sqrt{j(j+1)}\hbar, \quad j_z = m_j \hbar.$$

$m_j$  takes values of  $j, (j-1), \dots, -j$

- Spin quantum # - always  $\frac{1}{2}$ . We get:

$$j = l \oplus s = (l \pm 1/2)$$

- When  $l=0$ ,  $j=1/2$  (spin only).

# Angular momentum coupling in multi-electron atoms

- **Recall:** N – electron atom Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2$$

Where:

$$\hat{H}_0 = \sum_{i=1}^N \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + V_{\text{central}}(r_i) \right)$$

$$\hat{H}_1 = \sum_{i>j}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N V_{\text{central}}(r_i)$$

$$\hat{H}_2 = \sum_{i=1}^N \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i$$

# In the central field approximation:

- $H_1$  (non radial contribution) and  $H_2$  (spin orbit contribution) are ignored.
- $H_1$  are the non radial repulsion forces between the electrons – leads to LS coupling.  $H_2$  is negligible in small and medium atoms (proportional to  $Z^2$ ).
- In LS coupling, the individual electrons orbital angular momentum ( $l_i$ ) are summed to give a total angular momentum  $L$ . Same for spins to give  $S$ .

# LS coupling is related to the non radial e-e repulsion.

- The single electron angular momenta are solutions of the Schrodinger eqn. with a radial potential.
- Non radial repulsions causes that the angular momenta of the two repulsing electrons are no longer in an eigenstate.
- However these torques are internal and can not change the total angular momentum.

# Notation:

- Lower case quantum numbers ( $j, l, s$ ) refer to individual electrons in an atom.
- Upper case quantum numbers ( $J, L, S$ ) refer to angular momentum states of the whole atom.
- Due to residual electrostatic interactions - the terms:

$$L = \sum_i l_i \qquad S = \sum_i s_i$$

- Summation only on valence electrons.



# For each atomic term

- It is possible to define the total angular momentum:

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

- The different J has a different energy due to spin orbit interaction (of the atomic angular momenta):

$$\Delta E_{\text{so}} \propto -\mu_{\text{spin}}^{\text{atom}} \cdot B_{\text{orbital}}^{\text{atom}} \propto \mathbf{L} \cdot \mathbf{S}$$

- The SO interaction splits the LS terms to levels marked by J

# Short hand notations:

- Each level in the LS regime is marked by:

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

- $2S+1$  and  $J$  appear as numbers/
- $L$  appears as a letter:
  - $S$  implies  $L = 0$ ,
  - $P$  implies  $L = 1$ ,
  - $D$  implies  $L = 2$ ,
  - $F$  implies  $L = 3$ , etc.

# The terms:

- An example: a  ${}^2P_{1/2}$  term is an energy level with the quantum numbers:  $S=1/2$ ,  $L=1$  and  $J=1/2$ .

${}^3D_3$  -  $S=1$ ,  $L=2$  and  $J=3$ .

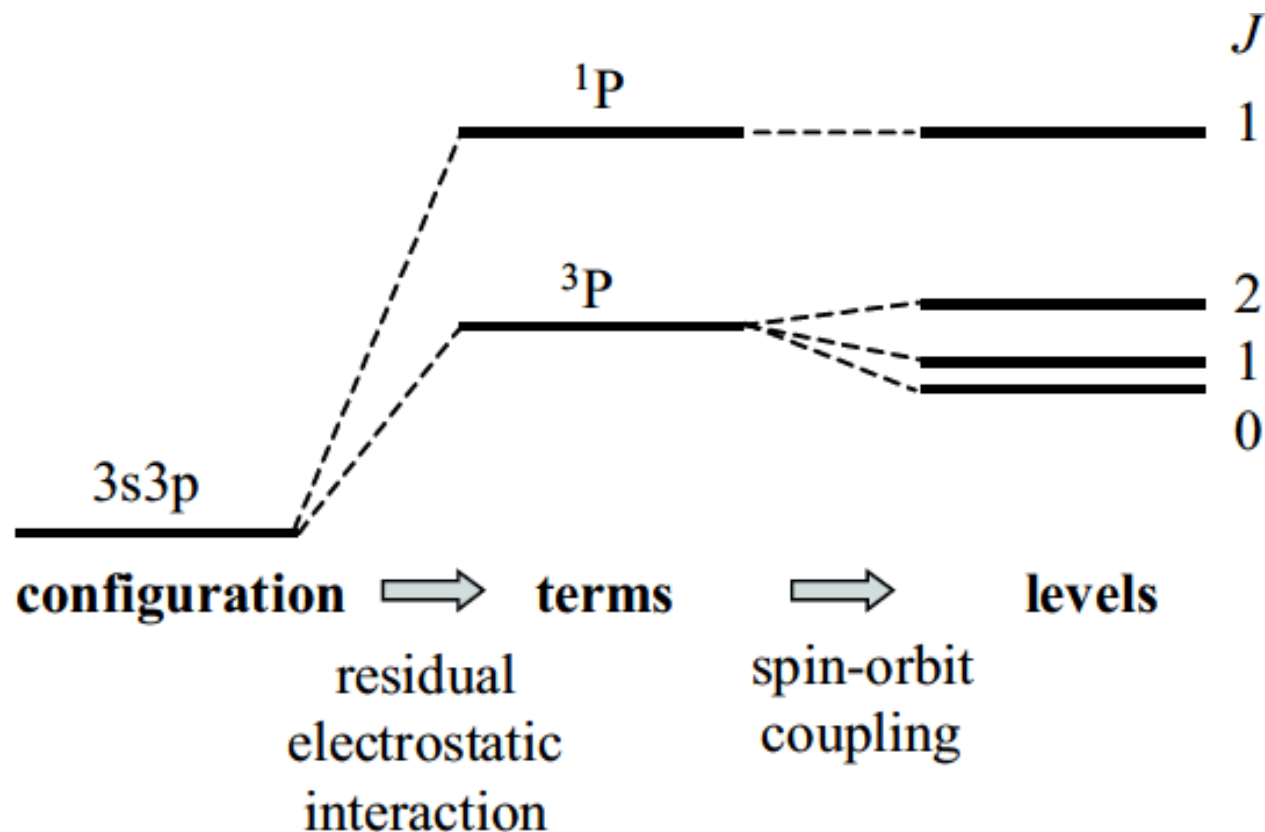
$2S+1$  is called the multiplicity – degeneracy due to spin - # of  $M_s$  states.  $S=0$  – singlet,  $S=1/2$  – doublet,  $S=1$  – triplet.

# Electronic configuration of Mg.

- One valance electron – s shell ( $l=0$ ), the other – p shell ( $l=1$ ).
- The LS terms:
  - $L = l_1 \oplus l_2 = 0 \oplus 1 = 1$ .
  - $S = s_1 \oplus s_2 = 1/2 \oplus 1/2 = 1$  or  $0$ .
- Two terms:  $^3P$  triplet and  $^1P$  singlet.
- For the triplet:  $J = L \oplus S = 1 \oplus 1 = 2, 1, \text{ or } 0$ .
- Three levels:  $^3P_2, ^3P_1$  and  $^3P_0$ .

# For the $^1P$ level:

- We get:  $J = L \oplus S = 1 \oplus 0 = 1$
- A single  $^1P$  level.
- We shall refer to the energetic order of these levels:



# Electric dipole selection rules in the LS coupling limit

- The selection rules (discussed already) depends also on angular momentum.
- Due to odd parity of the dipole operator, the parity must be changed, which implies  $\Delta l = \pm 1$  – in a transition between shells.

$\Delta L = 0, \pm 1$ , but  $L = 0 \rightarrow 0$  is forbidden

- In a single electron it is not possible to have  $\Delta l = 0$  but it is possible in many electron system:
- For example in:  $3p4p\ ^3P_1 \rightarrow 3p4s\ ^3P_2$ .

# Additional selection rules:

- In terms of total angular momentum:

$$J^{\text{initial}} = J^{\text{final}} + J^{\text{photon}}$$

(this refers to the component of  $J$  and not its magnitude).

$$\Delta J = 0, \pm 1, \text{ but } J = 0 \rightarrow 0 \text{ is forbidden}$$

The fifth selection rule:

$$\Delta S = 0.$$

Without spin – orbit coupling the spin can not change.

# Hund's rules

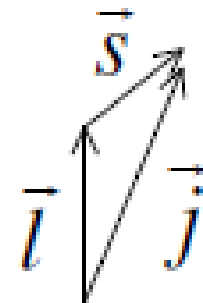
- The question – which of the possible terms is the ground state?
- It is determined by minimizing the energy of its valence electrons with the residual electrostatic and spin-orbit interactions.
- Applying Hund's laws is much simpler:
- **The term with the largest multiplicity (i.e. largest  $S$ ) has the lowest energy** (*spins tend to be parallel to minimize the exchange interaction*). *The Pauli exclusion principle – causes the two electrons to be far – minimizing the electrostatic repulsion*



# The other Hund's rules:

- For a given multiplicity, the term with the largest  $L$  has the lowest energy.
- This is due to spin orbit coupling: **Recall:**
- The total angular momentum:

$$\vec{j} = \vec{l} + \vec{s}$$



$$|\vec{j}|^2 = |\vec{l}|^2 + |\vec{s}|^2 + 2|\vec{l}||\vec{s}|\cos(l, s)$$

- And the SO interaction is:

$$V_{l,s} = \frac{a}{2\hbar^2} (|\vec{j}|^2 - |\vec{l}|^2 - |\vec{s}|^2)$$

# The last one:

- The level with  $J = |L - S|$  has the lowest energy if the shell is less than half full. If the shell is more than half full, the level with  $J = L + S$  has the lowest energy.
- To show that we discuss the sodium atom:

state  $3p$   $\rightarrow$   $j=3/2$  and  $V_{l,s} = \frac{a}{2} \left[ \frac{3}{2} \cdot \frac{5}{2} - 2 - \frac{1}{2} \cdot \frac{3}{2} \right] = \frac{a}{2}$

$\searrow$   $j=1/2$  and  $V_{l,s} = \frac{a}{2} \left[ \frac{1}{2} \cdot \frac{3}{2} - 2 - \frac{1}{2} \cdot \frac{3}{2} \right] = -a$

# The electronic configuration and the ground state of the first 11 elements

$Z$	Element	Configuration	Ground state
1	H	$1s^1$	$^2S_{1/2}$
2	He	$1s^2$	$^1S_0$
3	Li	$1s^2 2s^1$	$^2S_{1/2}$
4	Be	$1s^2 2s^2$	$^1S_0$
5	B	$1s^2 2s^2 2p^1$	$^2P_{1/2}$
6	C	$1s^2 2s^2 2p^2$	$^3P_0$
7	N	$1s^2 2s^2 2p^3$	$^4S_{3/2}$
8	O	$1s^2 2s^2 2p^4$	$^3P_2$
9	F	$1s^2 2s^2 2p^5$	$^2P_{3/2}$
10	Ne	$1s^2 2s^2 2p^6$	$^1S_0$
11	Na	$1s^2 2s^2 2p^6 3s^1$	$^2S_{1/2}$

# jj coupling

- The spin-orbit interaction gets larger as  $Z$  increases (*will be discussed*)
- In atoms with large  $Z$  (e.g. tin with  $Z = 50$ ) The SO coupling gets bigger than the residual electrostatic interaction. The orbital and spin angular momenta of the individual electrons are coupled first. The total  $J$  is the sum of the individual  $j$  of each electron.

$$j_i = l_i + s_i$$

$$J = \sum_{i=1}^N j_i$$

- The residual interaction is now a perturbation.