Chapt. 5 Atom with Many electrons--Pauli exclusion Principle

5.1. Spectra & energy levels of Helium

5.2. Coupling of two electrons

5.3. Pauli exclusion principle

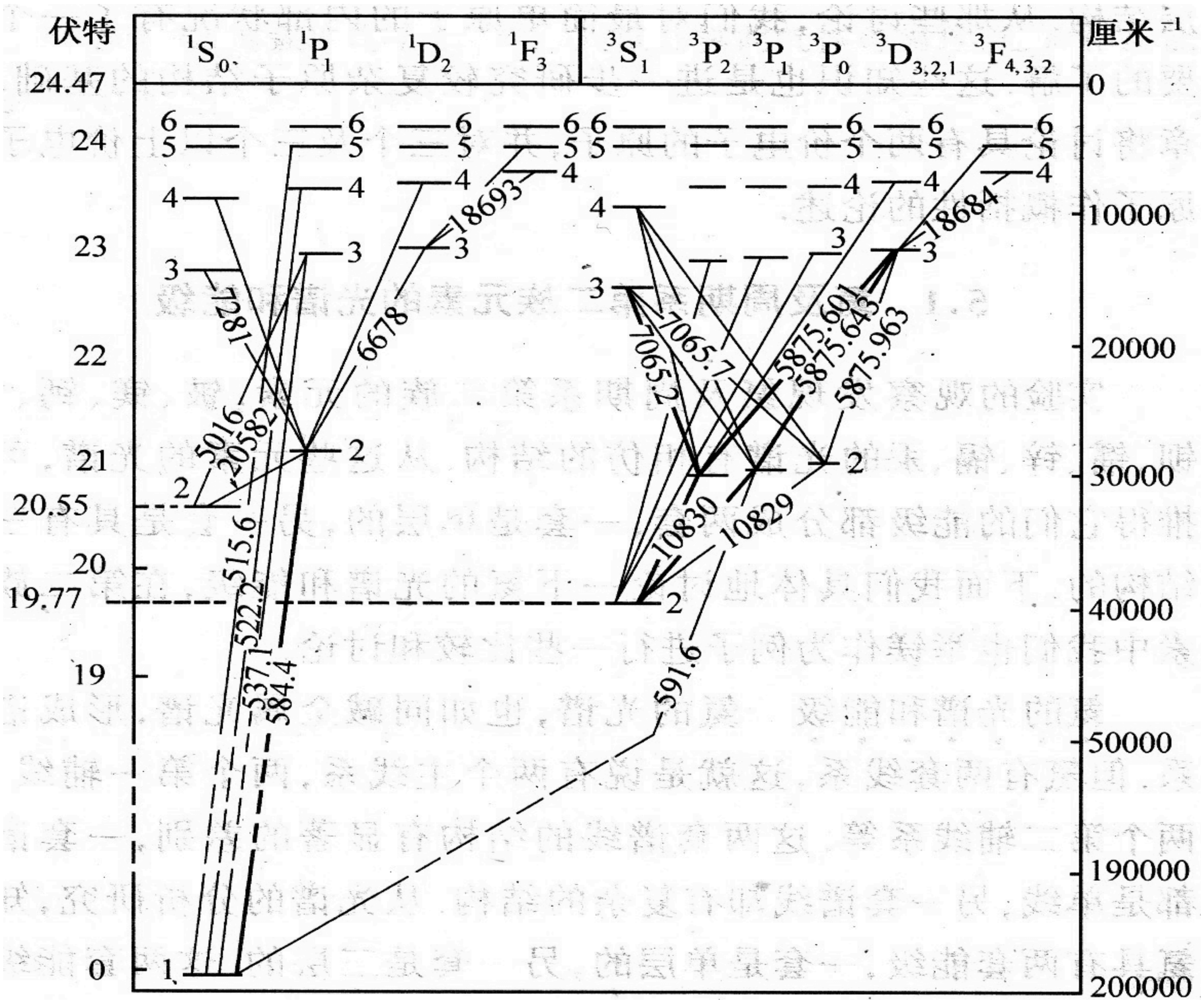
5.4. Periodic Table of elements

5.1. Spectra and Energy levels of Helium

- Spectra and energy level of Helium
- Electrons configuration
- Energy-level diagram

Spectra lines of Helium

- **Helium atom**
  - With 2 electrons
- Spectra of Helium
  - **Forming spectra line series**
  - **Two sets of spectra lines (each set has 4 series)**
  - **One set has only single lines, the other set has complex structure (triplet)**

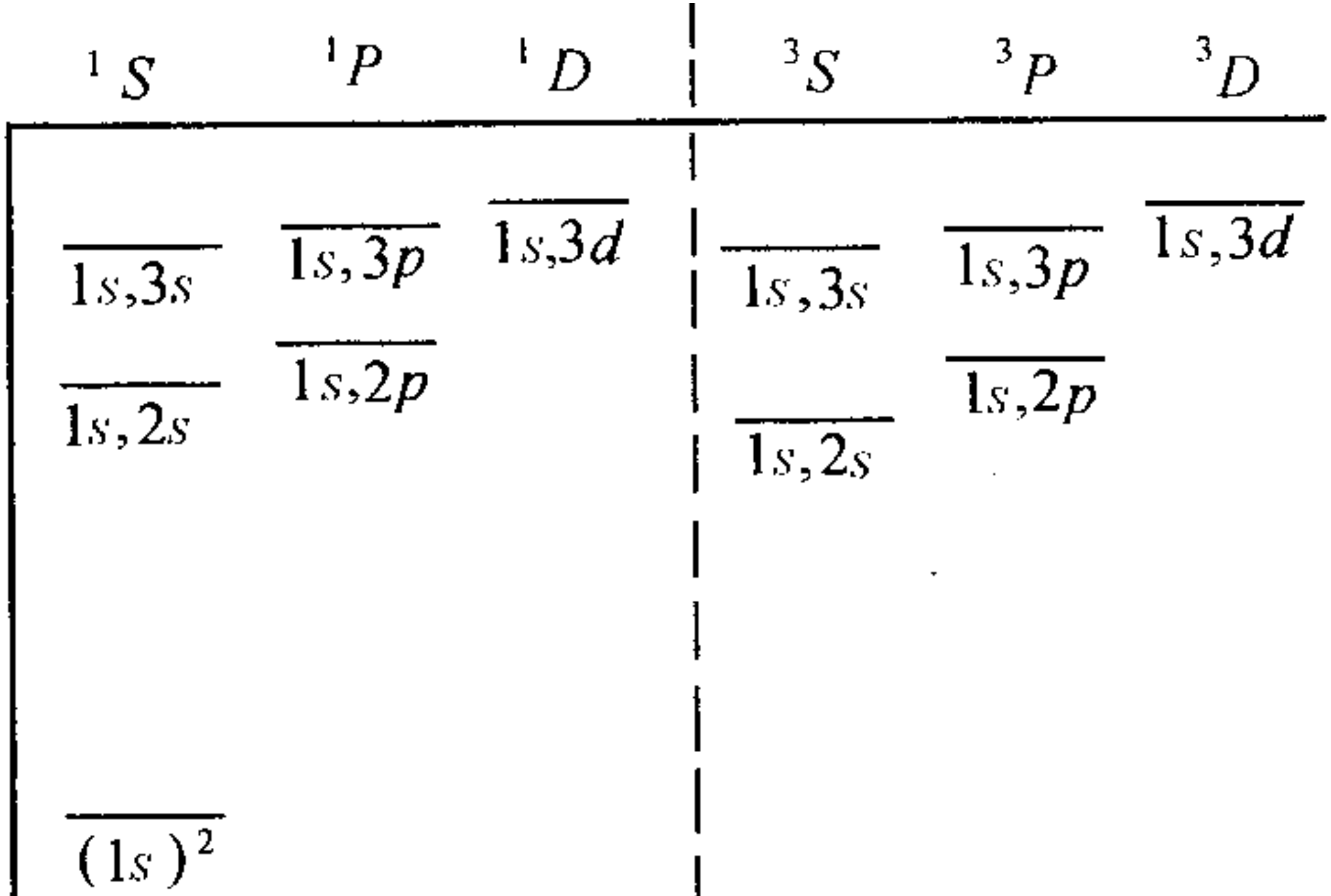


Energy levels of Helium

Energy levels of Helium

- Two sets: singlet， triplet, no transition between them
- Exists metastable states: long lifetime excited states
- The energy gap between the ground & 1st excited states 19.77ev is larger than that for H atom with largest ionization energy 24.58ev among all elements
- For the triplet states, there is no state with n=1

energy-levels for Helium



Ground state

$1s1s=(1s)^2$

Single e-excited state : one is in 1s, another e is excited state: 2s, 2p, 3s, 3p, 3d, …

5.2. The coupling of the 2 electrons

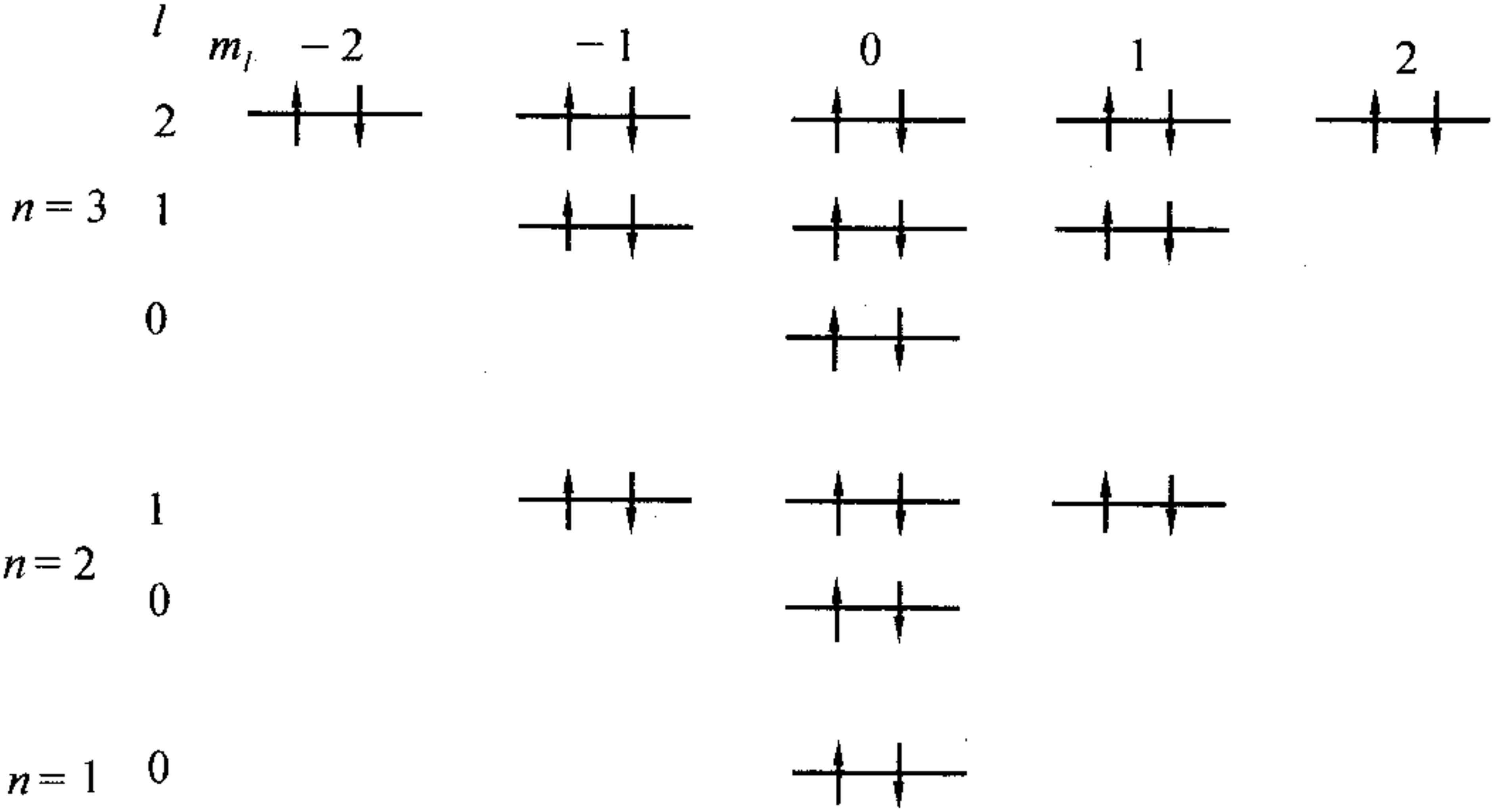
- Electrons configuration
- L-S & j-j coupling
- Coupling rules of 2 AM
- Selection rules
- Atomic state

5.2.1.Electrons Configurations

- Every electron's state in atom
- Electron's state by ***n*, *l***
- E. g
  - Ground state of Hydrogen :1s
  - Ground state of Helium is 1s1s=$(1s)^2$

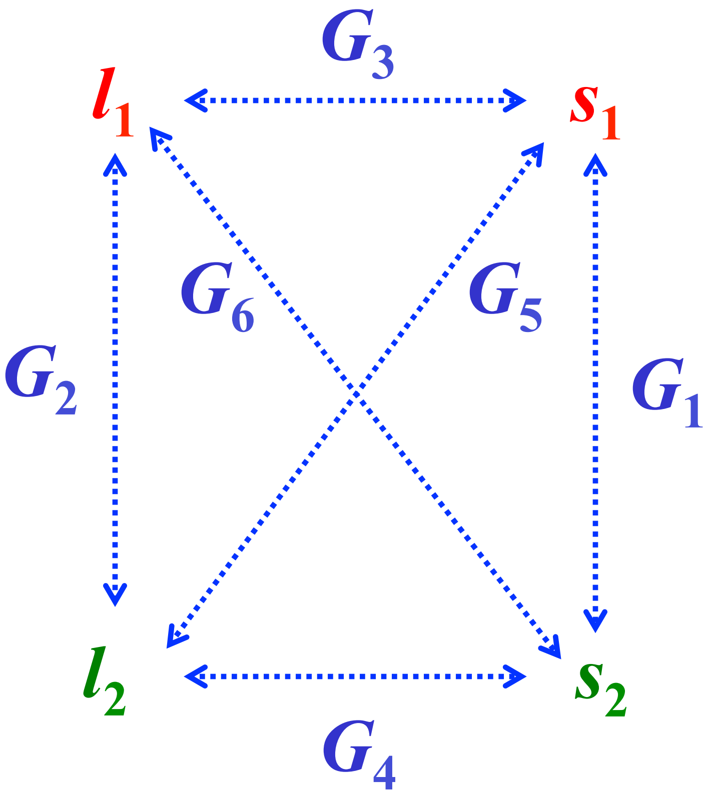
- **An electron configuration can has many configurations of atom**

5. 2. 1. electron's configurations



5.2.2. *L-S* & *j-j* coupling

- 6 combinations



l , s (μ) $\Leftrightarrow B \Leftrightarrow$ l , s (μ)

$G_1(s_1, s_2)$, $G_2(l_1, l_2)$, $G_3(s_1, l_1)$, $G_4(s_2, l_2)$, $G_5(s_1, l_2)$, $G_6(s_2, l_1)$

$G_5(s_1, l_2)$, $G_6(s_2, l_1)$ **negligiable**

- ***L-S*** **coupling**
  - $G_1, G_2 > G_3, G_4$

$$(s_1 s_2)(l_1 l_2) = (S, L) = J$$

- ***j-j*** **coupling**
  - $G_3, G_4 > G_1, G_2$

$$(s_1 l_1)(s_2 l_2) = (j_1 j_2) = J$$

stronger coupling has the priority than the weak case

L-S **atomic state** $^{2S+1}L_J$

j-j **atomic state** $(j_1, j_2)_J$

- **General** ***L-S***

$$(s_1 s_2 s_3 \cdots)(l_1 l_2 l_2 \cdots) = (S, L) = J$$

- **Genery** ***j-j***

$$(s_1 l_1)(s_2 l_2)(s_3 l_3)\cdots = (j_1 j_2 j_3 \cdots) = J$$

5.2.3. Coupling rules for 2 AM

- ***L_1, L_2*** → **total angular momentum *L***
- $\vec{L} = \vec{L}_1 + \vec{L}_2$

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

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

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

$$\boxed{l = l_1 + l_2, l_1 + l_2 - 1, \cdots, |l_1 - l_2|}$$

$$\boxed{L_{1z} = m_{l_1}\hbar}$$

$$\boxed{L_{2z} = m_{l_2}\hbar}$$

$$\boxed{L_z = m_l\hbar}$$

$$\boxed{m_l = m_{l_1} + m_{l_2}}$$

- Coupling rules of 2 AM

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

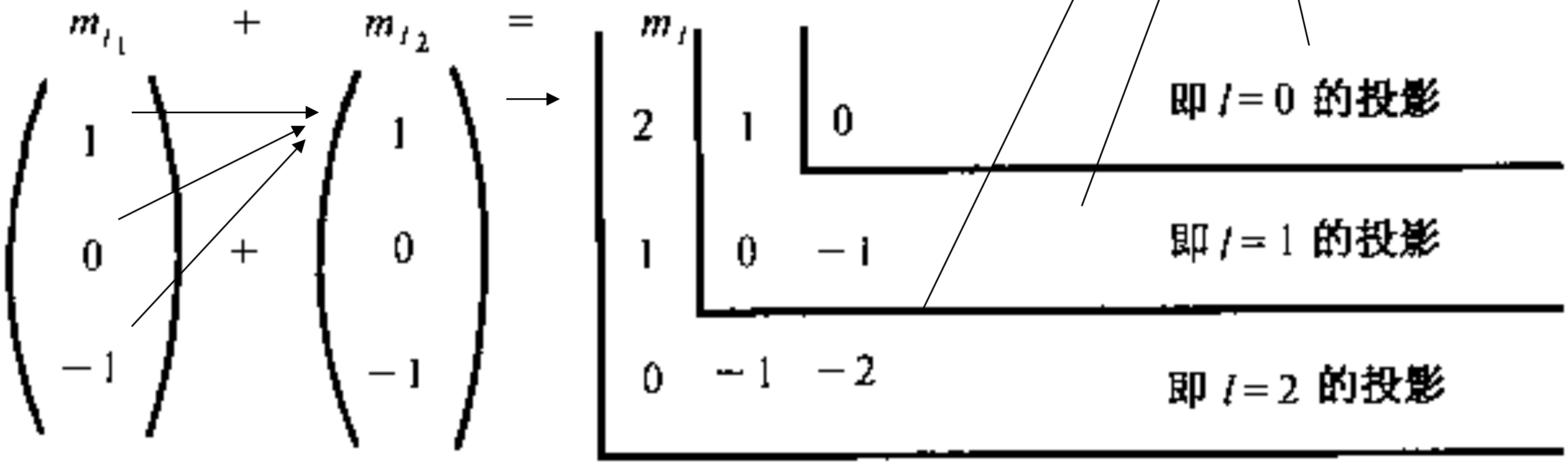
$$m_{l_1} = -1, 0, +1$$

$$m_{l_2} = -1, 0, +1$$

$$\boxed{l = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|}$$

$$l_1 = 1, l_2 = 1 \rightarrow l = 2, 1, 0$$

$$m_l = m_{l_1} + m_{l_2} \rightarrow$$



5.2.4. Selection Rules

- ***Selection rules for L-S* coupling**

$$\Delta S = 0$$

$$\Delta L = \pm 1$$

$$\Delta J = 0\,,\ \pm 1\ (\text{ except no } 0 \rightarrow 0\ )$$

- ***Selection rules for j-j coupling***

$$\Delta j_i = 0\,,\ \pm 1\ ;$$

$$\Delta J = 0\,,\ \pm 1\ (\text{except no } 0 \rightarrow 0\ )$$

- Why there is no cross transition between singlet and triplet
  - ***L-S* selection rule: $\Delta S = 0$**
  - Singlet $S=0$
  - triplet $S=1$

→

  - No cross transition

5.2.5. From electrons configuration to atomic state

- **Ex1:** ***L-S*** **coupling** ***sp***

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

$$\boxed{L_1 = \sqrt{l_1(l_1+1)}\hbar} \quad \boxed{L_2 = \sqrt{l_2(l_2+1)}\hbar} \quad \boxed{L = \sqrt{l(l+1)}\hbar}$$

$$\boxed{(s_1 s_2)(l_1 l_2) = (S, L) = J} \quad \boxed{l = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|}$$

$$l_1 = 0, l_2 = 1; \quad s_1 = s_2 = 1/2$$

$$l = 1; \quad s = \begin{cases} 1 & \rightarrow j = 2,1,0; \quad \rightarrow {}^3P_0, {}^3P_1, {}^3P_2 \\ 0 & \rightarrow j = 1 \quad \rightarrow {}^1P_1 \end{cases}$$

- **Ex2: *j-j* coupling *sp***

$$\boxed{(s_1 l_1)(s_2 l_2) = (j_1 j_2) = J}$$

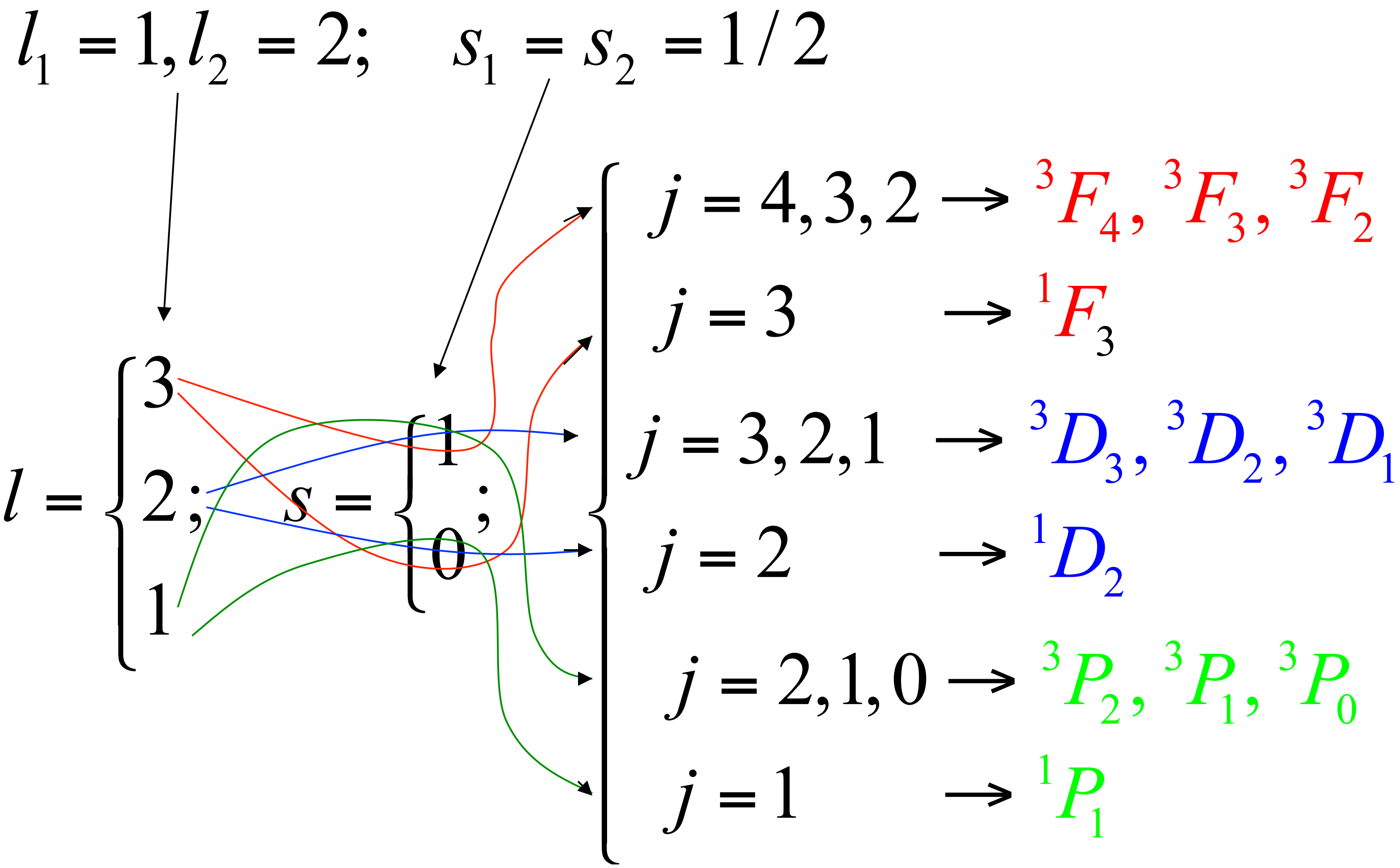
$$l_1 = 0, s_1 = 1/2; \quad l_2 = 1, s_2 = 1/2$$

$$j_1 = \frac{1}{2}; \quad j_2 = \begin{cases} \dfrac{1}{2} \to j = 1, 0; \to \left(\dfrac{1}{2}, \dfrac{1}{2}\right)_1, \left(\dfrac{1}{2}, \dfrac{1}{2}\right)_0 \\[2ex] \dfrac{3}{2} \to j = 2, 1; \to \left(\dfrac{1}{2}, \dfrac{3}{2}\right)_2, \left(\dfrac{1}{2}, \dfrac{3}{2}\right)_1 \end{cases}$$

The same *J* data

The same number of atomic states

• *Ex3. L-S* **coupling** ***pd***



$$l_1 = 1, l_2 = 2; \quad s_1 = s_2 = 1/2$$

$$l = \begin{cases} 3 \\ 2; \\ 1 \end{cases} \quad s = \begin{cases} 1 \\ 0 \end{cases};$$

$$j = 4, 3, 2 \rightarrow {}^3F_4, {}^3F_3, {}^3F_2$$

$$j = 3 \rightarrow {}^1F_3$$

$$j = 3, 2, 1 \rightarrow {}^3D_3, {}^3D_2, {}^3D_1$$

$$j = 2 \rightarrow {}^1D_2$$

$$j = 2, 1, 0 \rightarrow {}^3P_2, {}^3P_1, {}^3P_0$$

$$j = 1 \rightarrow {}^1P_1$$

- **Eg4: *L-S* coupling *ss***

$$^1S_0, \ ^3S_1$$

- **Eg5: *L-S* coupling *pp***

$$^1S_0, \ ^3S_1; \ ^1P_1, \ ^3P_{2,1,0}; \ ^1D_2, \ ^3D_{3,2,1}$$

L-S **versus** ***j-j***

- ***L-S works for light atoms and lower excitations***
- ***j-j works for heavy atoms and higher excitations***

5.3. Pauli exclusion principle

- Statement of Pauli exclusion Pinciple
- Application examples
- Atomic states from equivalent electrons

5.3.1. Statement of Pauli exclusion Principle (PEP)

- **Electron-state is described by 4 quantum numbers(QN) ：n、l、 m and m_s**
  - **n： electrons' energy levels from low to high energy n= 1, 2, 3, …**
  - **l ： Orbital angular momentum . with fixing n, l = 0, 1, 2, …, n -1 ;**
  - **Magnetic QN m： for a fixing l ， m takes 2l+1 possible values ， m = 0, ±1, ±2, …, ± l;**
  - **Spin magnetic QN ms： spin AM along z ， ms= ½ (up)， ms =−1/2 (down)。**

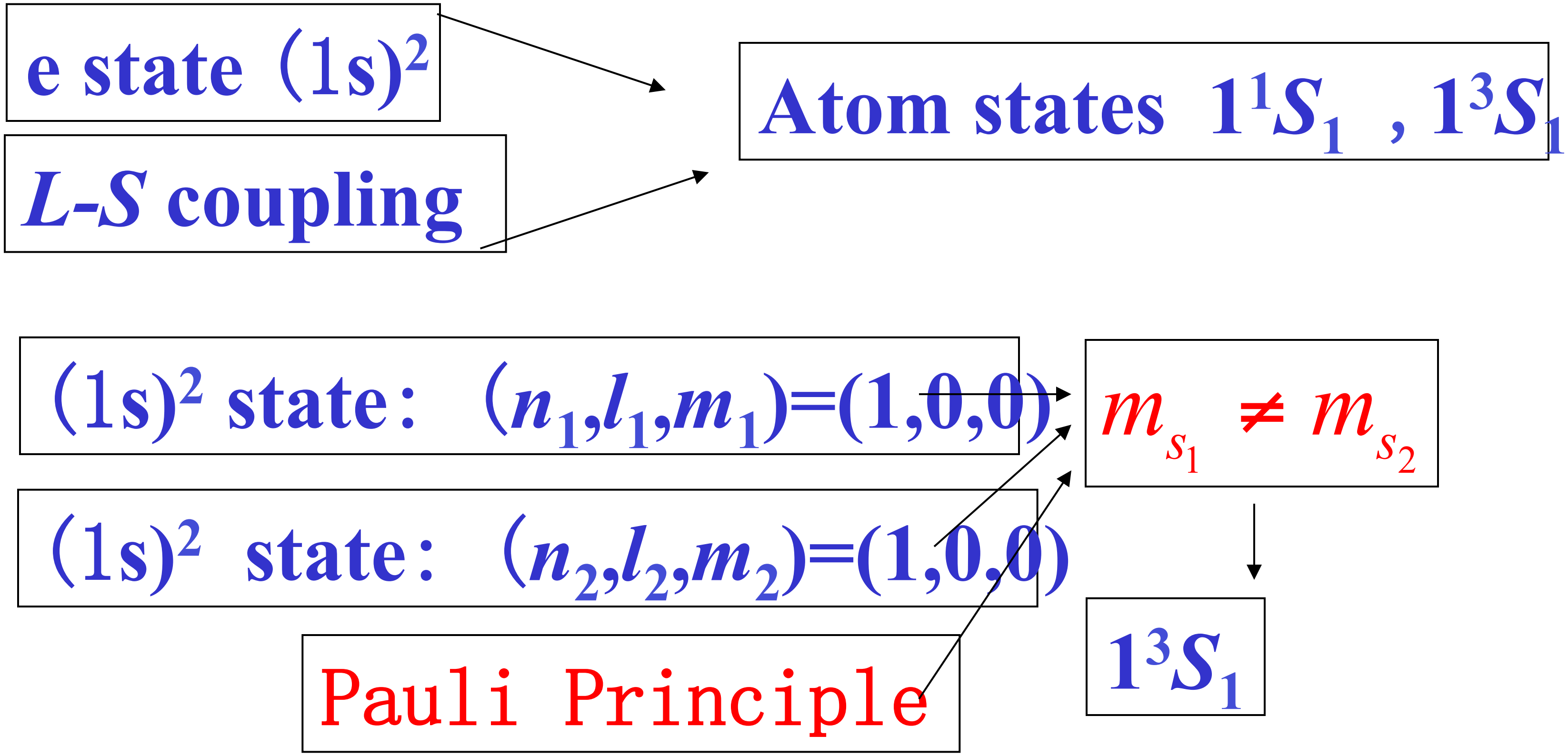
Pauli exclusion principle

- In a system composed of fermions. There can not be 2 or more than 2 fermions in completely the the same state, namely take the same set of quantum numbers (n, l, m, m_s)

One electron⇔ one state(n, l, m, m_s)

5.3.3 Examples

- **Ex1: Why there is no (1s1s)→ 1^3S_1 state？**



e state $(1s)^2$

L-S coupling

Atom states 1^1S_1 , 1^3S_1

$(1s)^2$ state： $(n_1,l_1,m_1)=(1,0,0)$

$(1s)^2$ state： $(n_2,l_2,m_2)=(1,0,0)$

Pauli Principle

$m_{s_1} \neq m_{s_2}$

1^3S_1

- Ex2： **equivalents electrons**： **Why the energy of triplet is lower than the singlet state?**

- Equivalents electrons

$$n_1=n_2,\ l_1=l_2$$

$$\boxed{m_{s_1}=m_{s_2}\rightarrow m_1\neq m_2}$$

triplet

Large distance, lower potential

Example 3

- Why atoms have almost the same sizes?

Orbit radius with Z protons $r = a_1 \frac{n^2}{Z}$

$n = \text{constant},\ Z \uparrow \rightarrow r \downarrow$

PEP→**finite numbers of electron**

↓

Z↑→more orbits

⇒size of atoms are almost identical

5.3.4.Atomic states from equivalent electrons

- Equiv electrons: electrons with same ***n* , *l***
- PEP→the atomic states from equiv. electrons are less than that from non-equiv. ones
- 1s2s e state→ atom states $^1S_0, {}^3S_1$

  1s1s → atom states $^1S_0, {}^3\cancel{S}_1$
- 2p3p e state →atom states

  $$^1S_0, {}^3S_1;\ {}^1P_1, {}^3P_{2,1,0};\ {}^1D_2, {}^3D_{3,2,1}$$

  2p2p→ atom states

  $$^1S_0, {}^3\cancel{S}_1;\ {}^1\cancel{P}_1, {}^3P_{2,1,0};\ {}^1D_2, {}^3\cancel{D}_{3,2,1}$$

- **$3d4d$ eState→atom states**

$${}^1S_0,\ {}^3S_1;\ {}^1P_1,\ {}^3P_{2,1,0};\ {}^1D_2,\ {}^3D_{3,2,1};\ {}^1F_2,\ {}^3F_{4,3,1};\ {}^1G_2,\ {}^3G_{5,4,3}$$

$3d3d$→amot states

$${}^1S_0,\ {}^3\cancel{S}_1;\ {}^1\cancel{P}_1,\ {}^3P_{2,1,0};\ {}^1D_2,\ {}^3\cancel{D}_{3,2,1};\ {}^1\cancel{F}_2,\ {}^3F_{4,3,1};\ {}^1G_2,\ {}^3\cancel{G}_{5,4,3}$$

- **Method to obtain atomic states (1)**

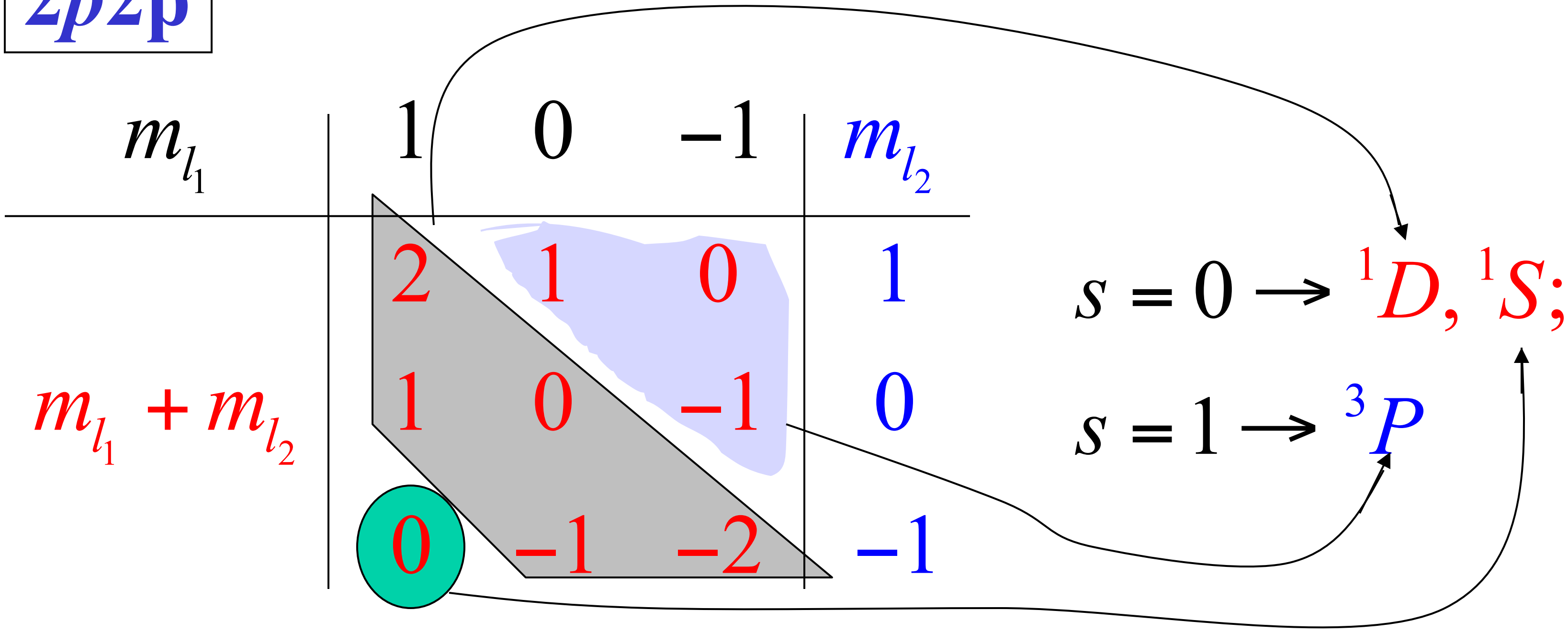
$\boxed{1s1s}$

$$\begin{array}{r|c|c} m_{l_1} & 0 & m_{l_2} \\ \hline m_{l_1}+m_{l_2} & 0 & 0 \end{array} \rightarrow {}^1S$$

$$\boxed{\begin{array}{l} S=0,\quad L\ \textit{along diagonal line (down)} \\ S=1,\quad L\ \textit{along the diagonal line (up)} \end{array}}$$

- **Obtain atomic states from equiv . electrons2**

2*p*2p

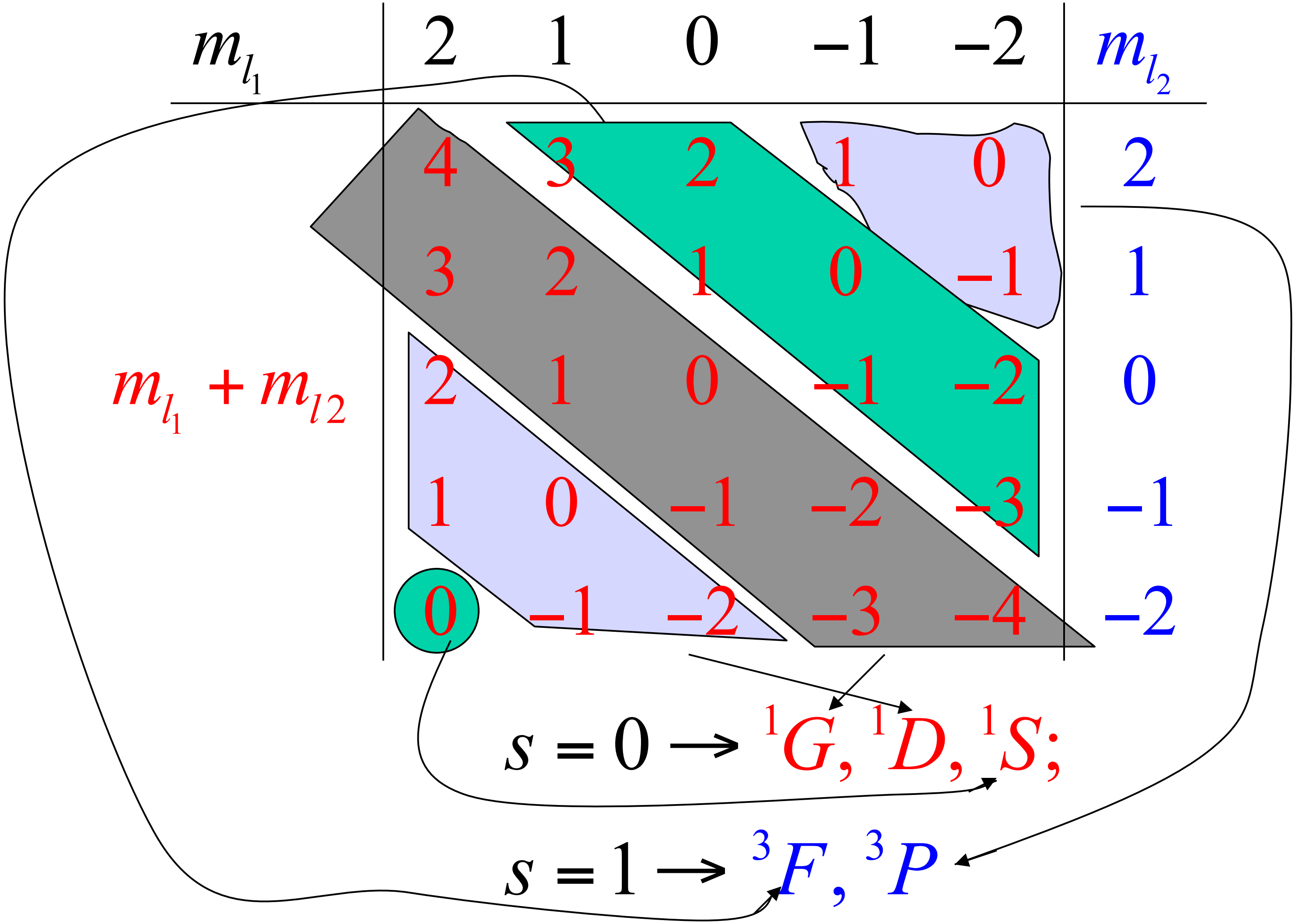


$$\begin{array}{c|ccc|c} m_{l_1} & 1 & 0 & -1 & m_{l_2} \\ \hline & 2 & 1 & 0 & 1 \\ m_{l_1}+m_{l_2} & 1 & 0 & -1 & 0 \\ & 0 & -1 & -2 & -1 \end{array}$$

$s = 0 \rightarrow {}^1D, {}^1S;$

$s = 1 \rightarrow {}^3P$

- **3d3d**



m_{l_1}	2	1	0	−1	−2	m_{l_2}
	4	3	2	1	0	2
	3	2	1	0	−1	1
$m_{l_1}+m_{l2}$	2	1	0	−1	−2	0
	1	0	−1	−2	−3	−1
	0	−1	−2	−3	−4	−2

$$s = 0 \rightarrow {}^1G, {}^1D, {}^1S;$$

$$s = 1 \rightarrow {}^3F, {}^3P$$

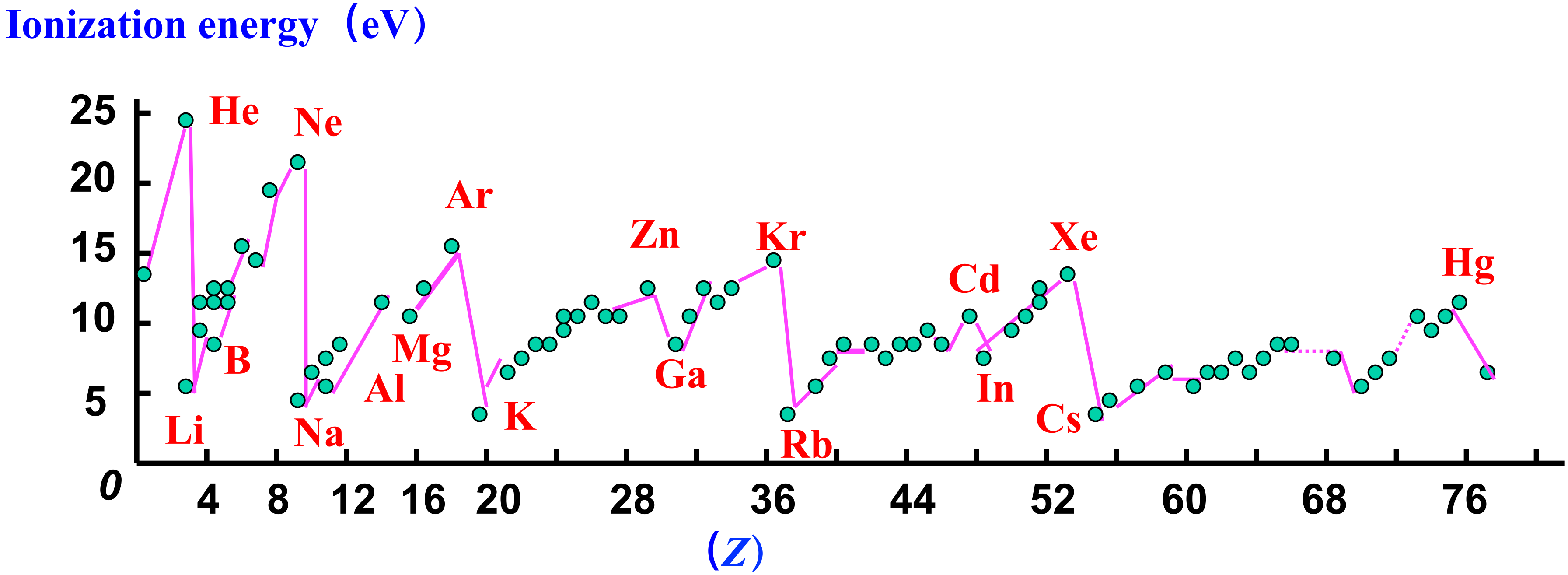
5.4. Periodic Table of elements

- **The periodicity of the properties of elements**
- **The number of electrons in the shells**
- **The order of the shells**
- **Electrons configuration→gound state of atoms**

5. 4. 1. The periodicity of the properties of elements

- The properties of elements change with Z with a periodic behavior
- **With lowest electrons energy, an atom is in the ground state**
- **E.g. ionization energy changes with Z**

  the energy needed to pull one electron off an atom



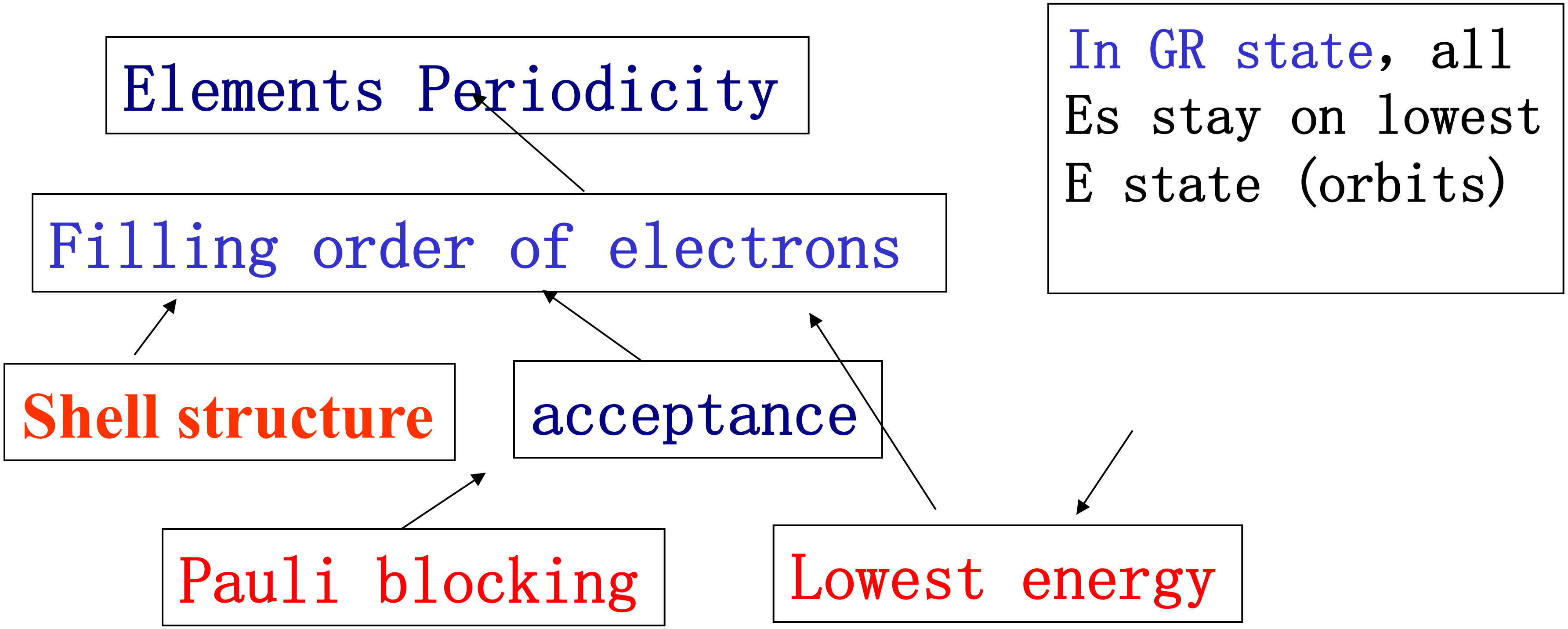
ionization energies versus atomic number

Peaks locate at magic numbers :**2,10,18,36, 54,86**. Hints of origin periodic properties of elements(?)

Periodic table

			Magic numbers
1	H (Z=1)	He(Z = 2)	2
II	Li(Z=3)	Ne(Z = 10)	10
III	Na(Z=11)	Ar(Z = 18)	18
IV	K (Z=19)	Kr(Z = 36)	36
V	Rb(Z=37)	Xe(Z = 54)	54
VI	Cs(Z=55)	Rn(Z = 86)	86
VII	Fr(Z=87)	Z=107,109（108）	

- Understanding the PT



Elements Periodicity

Filling order of electrons

Shell structure

acceptance

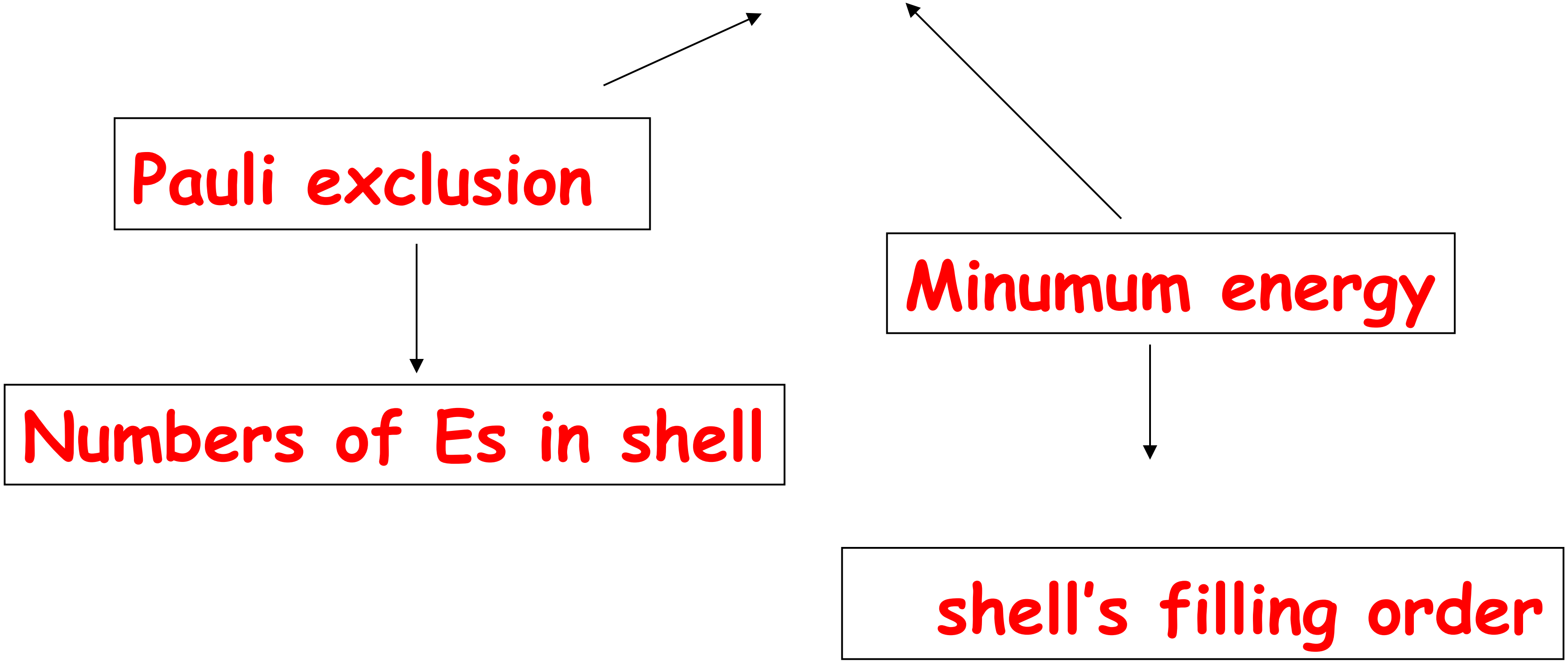
Pauli blocking

Lowest energy

In GR state, all Es stay on lowest E state (orbits)

5.4.2.Number of Electrons in shells

- Shell-structure, filling orders→**periodic behaviors**
- Electrons states are determined by two rules:



Pauli exclusion

Numbers of Es in shell

Minumum energy

shell's filling order

- For electrons state, one needs 4 QNs

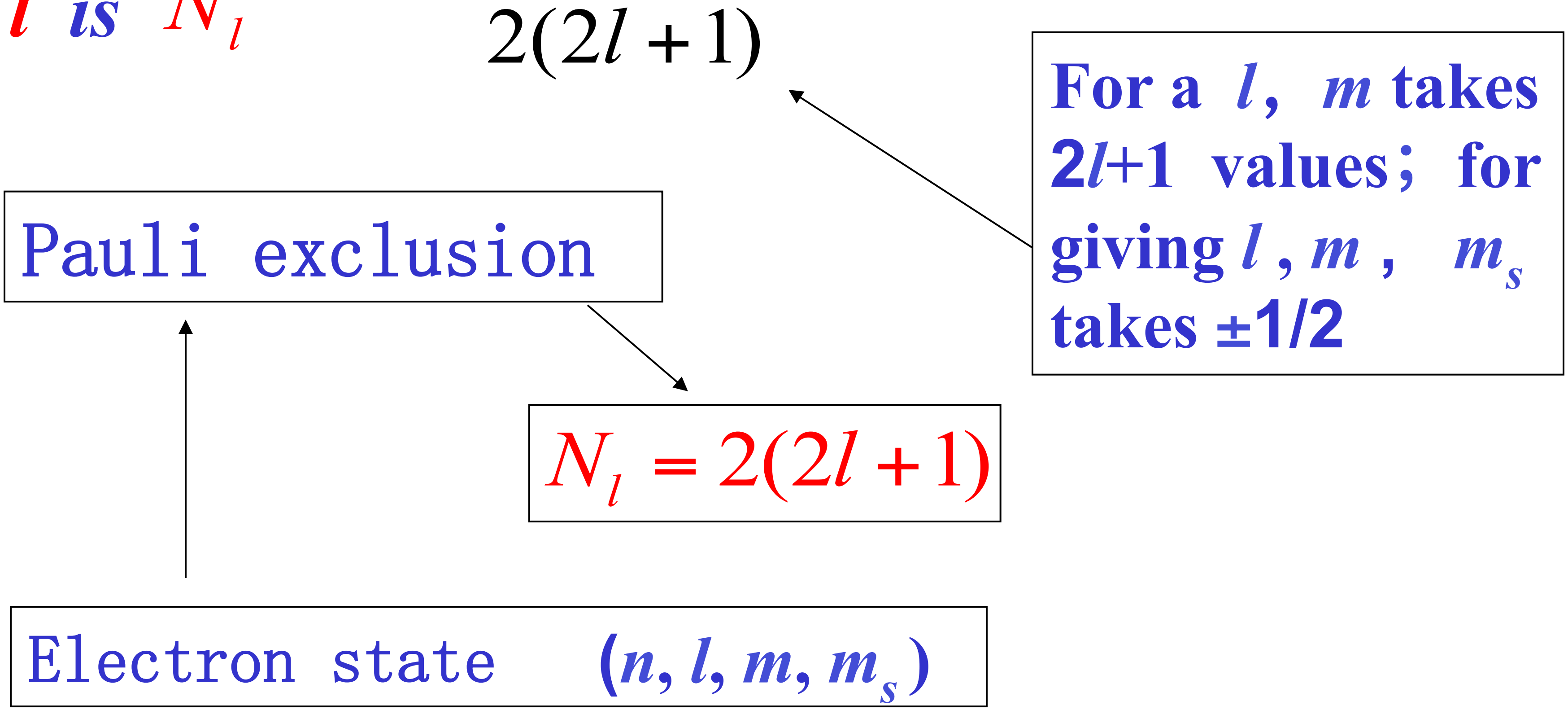
  n、l、m、m_s

- Classification of atomic states
  - Divide atomic states into shells using n , the same n Es form a shell
  - $n = 1, 2, 3, 4, 5,$ named K, L, M, N, O, … shells
  - Electrons on those shells are called K, L, M , N, O… electrons

subshells

- In the same shell *n*, there are any value of *l* （*l* = 0, 1, 2 ,…, *n* -1） ,each shell is divided into *n* sub-shells
- for *l* = 0, 1, 2, 3, 4, 5, …sub-shells are denoted by *s, p, d, f, g, h,* and so on
- Electrons on those subshell are called, *s* , *p, d, f, g, h*… electrons

- The maximum N of Es allowed in subshell *l* is N_l



$2(2l+1)$

For a *l*, *m* takes 2*l*+1 values; for giving *l*, *m*, m_s takes ±1/2

Pauli exclusion

$$N_l = 2(2l+1)$$

Electron state (n, l, m, m_s)

- Maximum Ns of Es in shell n: N_n

States number

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

Ging n, l takes (l = 0, 1, 2 ,…., n -1) values

Pauli exclusion

$$N_n = 2n^2$$

One lectron⇔ one state (n, l, m, m_s)

n	1	2	3	4	5
壳层	***K***	***L***	***M***	***N***	***O***
支壳层	**1*s***	**2*s*,2*p***	**3*s*,3*p*,3*d***	**4*s*,4*p*,4*d*,4*f***	**5*s*,5*p*,5*d*,5*f*,5*g***
N_l	2	2, 6	2, 6, 10	2, 6, 10, 14	**2,6,10,14,18**
N_n	2	8	18	32	50
$\sum N_n$	2	10	28	60	110

- Atomic state with full-filled *l* **sub-shell is** $^{1}S_{0}$
  - **E.g: full –filled** $2p$ ***state is*** $^{1}S_{0}$

n	l	m_l	m_s
2	1	-1	$1/2$
2	1	-1	$-1/2$
2	1	0	$1/2$
2	1	0	$-1/2$
2	1	1	$1/2$
2	1	1	$-1/2$

$$\boxed{N_l = 2(2l+1) = 6)}$$

$$\sum m_l = 0 \rightarrow M = 0 \rightarrow L = 0$$

$$\sum m_S = 0 \rightarrow M_S = 0 \rightarrow S = 0$$

$$L = 0, S = 0 \rightarrow J = 0$$

→**atomic state** $^{1}S_{0}$

- Atomic state for equivalent electrons
  - p **and** p^5 **have the same atomic state**

$$p:{}^{2S_1+1}(L_1)_{J_1} \qquad p^5:{}^{2S_2+1}(L_2)_{J_2}$$

$\boxed{p \text{ subshell: } N_l=6}$

$\boxed{\textit{Full-filled } p \textit{ shell : } {}^1S_0}$

$$\rightarrow \check{S}_1+\check{S}_2=0, \check{L}_1+\check{L}_2=0, \check{J}_1+\check{J}_2=0$$

$$\rightarrow S_1=S_2, L_1=L_2, J_1=J_2$$

– d^2 **and** d^8 **have the same atomic state**

$$d^2 : {}^{2S_1+1}(L_1)_{J_1} \qquad d^8 : {}^{2S_2+1}(L_2)_{J_2}$$

d subshell: $N_l = 10$

Full filled d subshell : $^1S_0$

$$\rightarrow \check{S}_1 + \check{S}_2 = 0, \check{L}_1 + \check{L}_2 = 0, \check{J}_1 + \check{J}_2 = 0$$

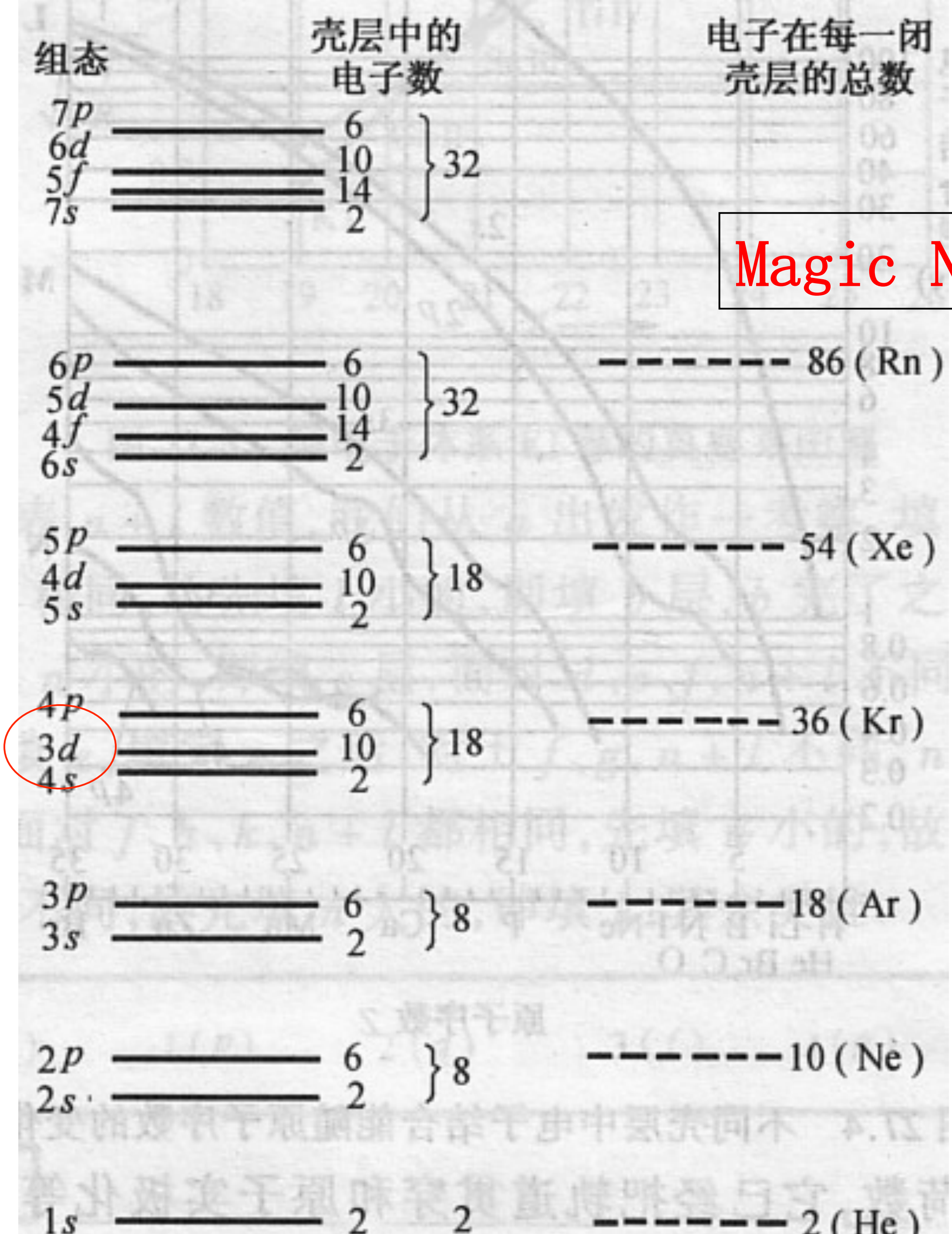
$$\rightarrow S_1 = S_2, L_1 = L_2, J_1 = J_2$$

5.4.3. The order of shells

- Minimum energy principle→shell order
  - GR state atom, electron fills the shell with ME; for the same shell, it fills the sub-shell with ME first
  - The energy order determines the Es filling order

  - *Do states with the same n* **(same shell), have close energies ?**

- Due to orbits penetration , and atomic core polarization→**E depends on *l* also**
- Redefine shells
  - **States with close energies belong to a shell, which may have states with different *n***
- Energy orders of shells & subshells



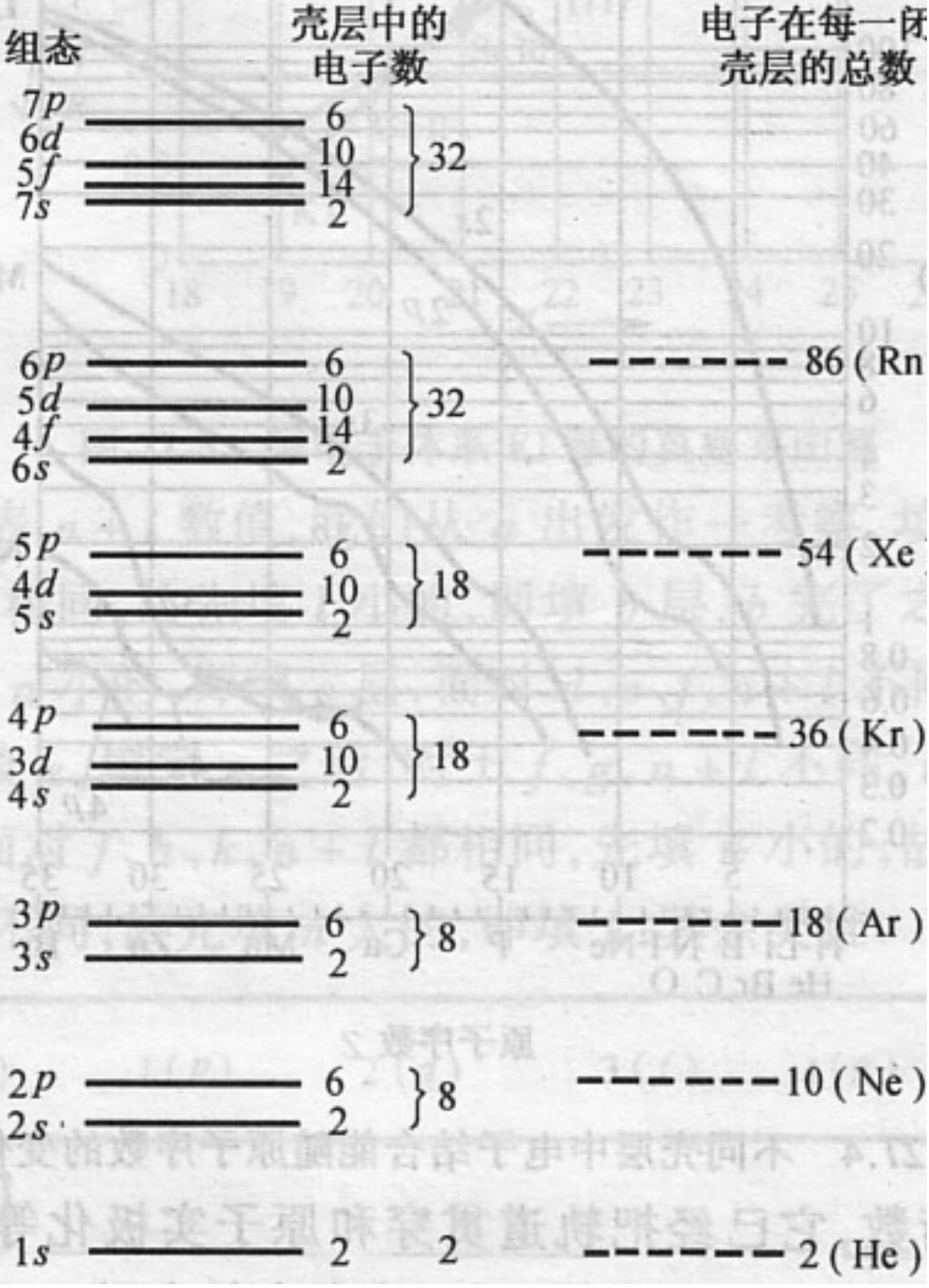
Magic N

Shell structure, Es
Filling order

↓

Periodicity

Each period starts new subshell filling,the Ns of Es in external subshell have periodic behavior


组态
壳层中的电子数
电子在每一闭
壳层的总数
7p 6
6d 10
5f 14
7s 2
32
6p 6
5d 10
4f 14
6s 2
32
86 (Rn
5p 6
4d 10
5s 2
18
54 (Xe
4p 6
3d 10
4s 2
18
36 (Kr)
3p 6
3s 2
8
18 (Ar)
2p 6
2s 2
8
10 (Ne)
1s 2
2
2 (He)

5.4.3. Order of shells

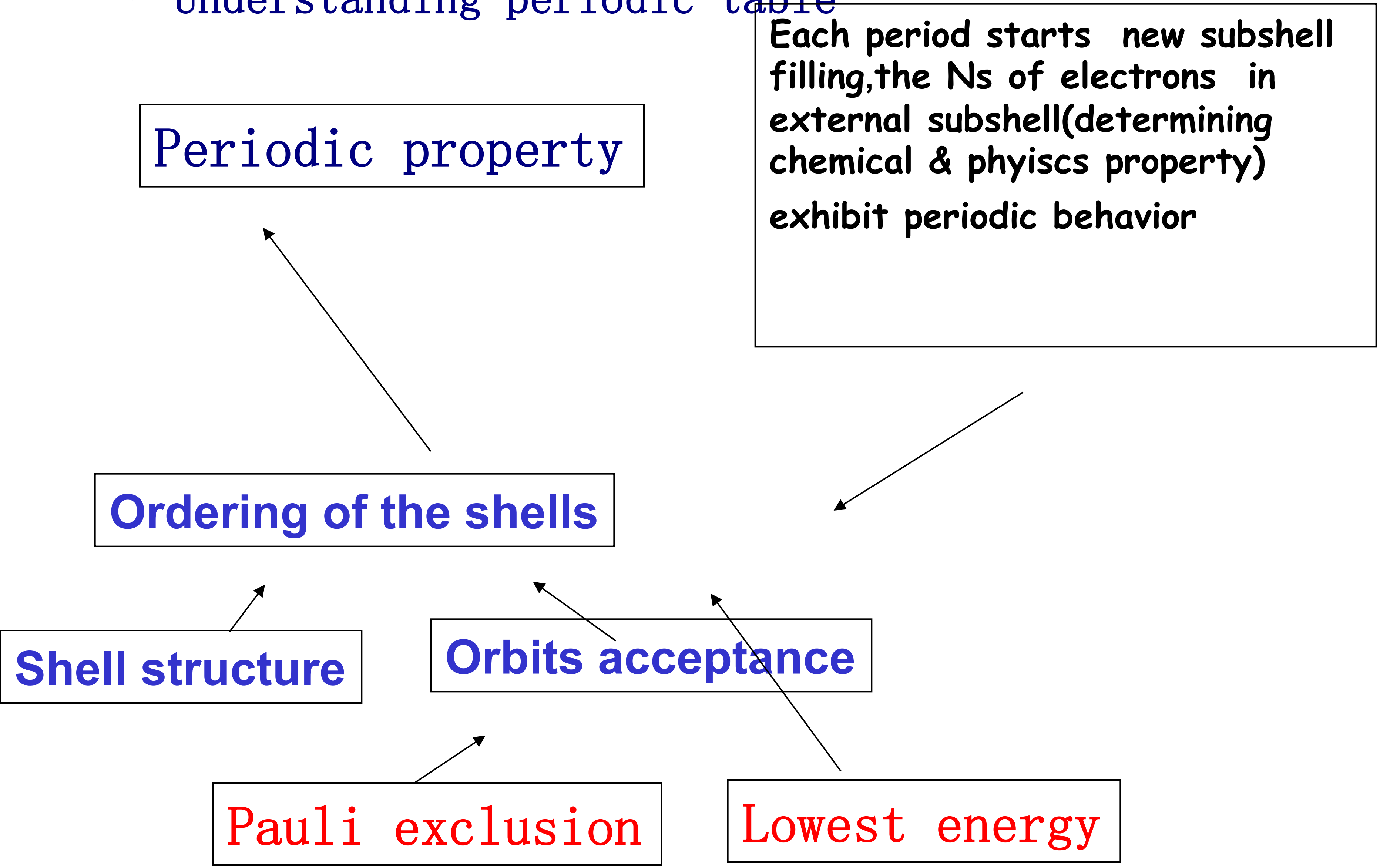
- **Why the energy of 4*s is lower than that of* 3*d?***

One has strong orbit penetration and atomic core polarization , while other almost no orbit penetration and polarization

$$E_{nl}=-1/2\ m\ c^2\ a^2\ Z^{*2}_{nl}/n^2$$

4*s with lower E; 3d with higher E*

- Understanding periodic table



Each period starts new subshell filling,the Ns of electrons in external subshell(determining chemical & phyiscs property)

exhibit periodic behavior

Periodic property

Ordering of the shells

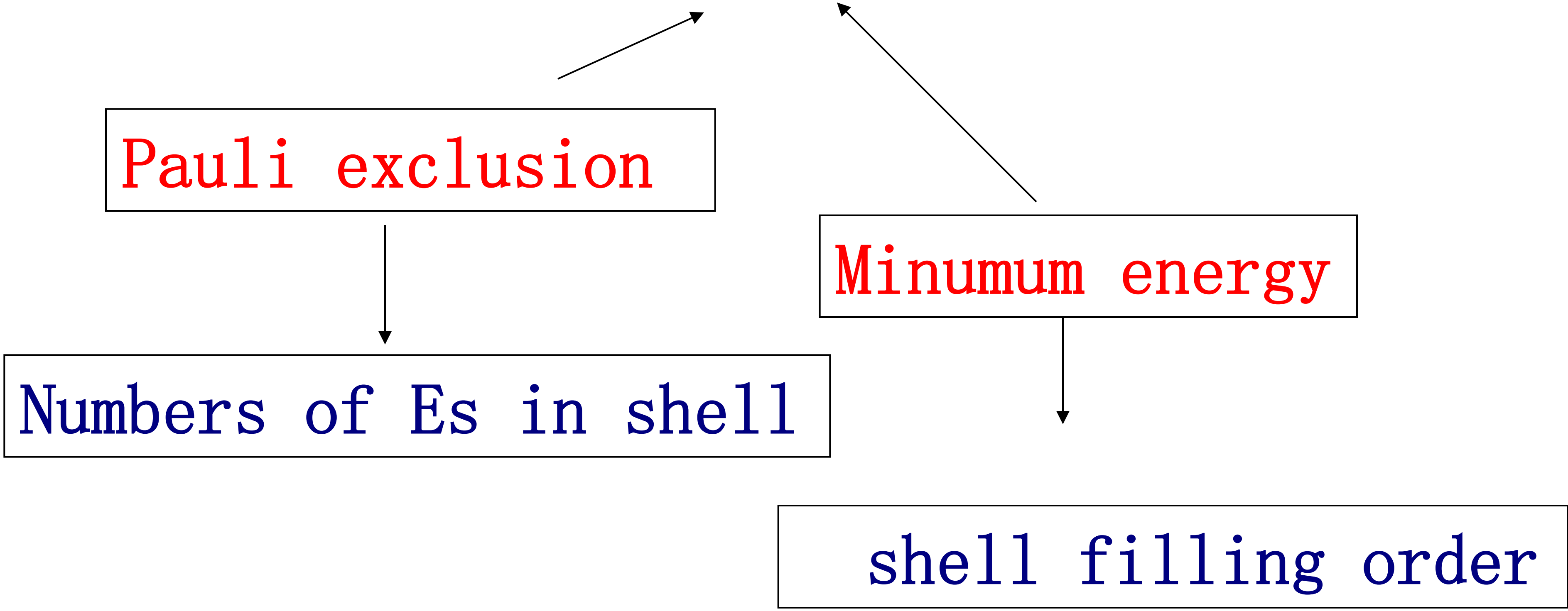
Shell structure

Orbits acceptance

Pauli exclusion

Lowest energy

- **Shell structure,** Es filling order→periodic behaviors
- Electrons states are determined by two rules:



5. 4. 4. Es' configurations→GR state of Es（1）

- **Es configuration;**filling order →atomic states

A Es state→several atomic states

e.g: 2*p*3*p*→ Atomic states

$$^1S_0,\ ^3S_1;\ ^1P_1,\ ^3P_{2,1,0};\ ^1D_2,\ ^3D_{3,2,1}$$

- **Giving Es state→determine atoms' GR state** ？

5.4.4. Atomic ground states

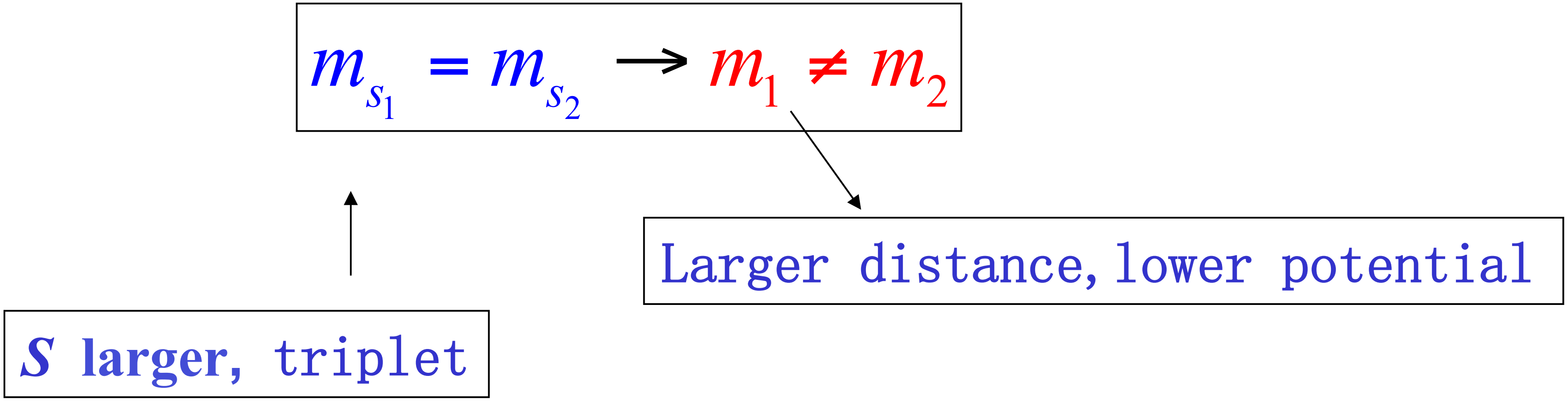
- **Hund's rule** (for *L-S* coupling)
  - **For a giving Es config. The larger the *S*, the lower of the energy of the state, for the same S,the larger the l, the lower the energy ;**
  - **For equivalent Es,*nl^{v}*: with the same l, when $v < (2l+1)$ (half shell), the smaller the *J, the lower the energy*(normal order)； when $v > (2l+1)$, the larger the *J*, the lower the energy (reversed order).**

- **With full-filled subshell, *m* and *m_s* takes positive & negative values in pairs , the total S、L , J equal to zero, GR state is** $^1S_0$

- **With incomplete-filled subshell, the atomic states are determied by the Es at incomplete filled subshell**

- **Understand Hunt’s rules**
  - **For the same Es configuration, why the larger the S, the lower the energy is？**

Equivalent 2 electrons ：$n_1=n_2, l_1=l_2$

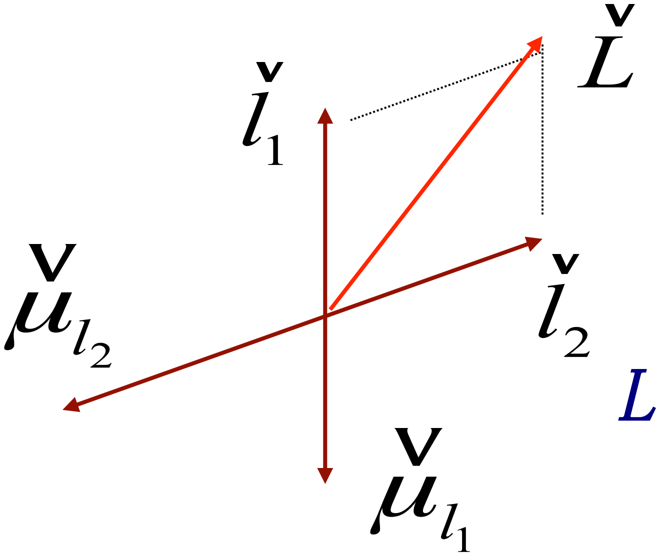


$m_{s_1} = m_{s_2} \rightarrow m_1 \neq m_2$

Larger distance, lower potential

S **larger,** triplet

- **for the same S,the larger the l, the lower the energy , Why?**



$$\Delta E = -\vec{\mu}_{l_2}\cdot\overset{\check{\mu}_{l_1}}{\overset{\swarrow}{\vec{B}_{l_1}}} \sim -\cos(\vec{l}_1\cdot\vec{l}_2)$$

L bigger→ $(\vec{l}_1,\vec{l}_2)$ smaller angle

→ lower energy

- What’ s the ground state of He state
  Helium (z=2)
  - **Electrons configurarion: ?**
  - **Ground state?**

Ground state of C atom

for C (Z=6)

Es config: $2p^2$ **;** $\nu < (2l+1)$ → **normal order**

→**atomic states** $^1D, ^1S; ^3P_{0,1,2}$

The larger S, lower energy → $^3P_{0,1,2}$ **lower**

The smaller J, the lower energy

→***GR state of C is*** $^3P_0$ **lowest**

Ground state of Oxygen atom

O atom Z=8

Es config: $2p^4$; $\nu > (2l+1)$ → **reversed order**

→**atomic states** $^1D, ^1S; ^3P_{0,1,2}$

The larger S, lower energy → $^3P_{0,1,2}$ **lower**

Reversed order, the largerJ, the lower energy

→*GR state of O is* $^3P_2$ **lowest**

GRS of **Li, Na, K, Cu, Ag, Au** atoms

Electrons configuration : *ns*

Ground state of those atom is

$$^{2}S_{1/2}$$

Agrees with Stern-Gerlach experiment

Landes interval rule

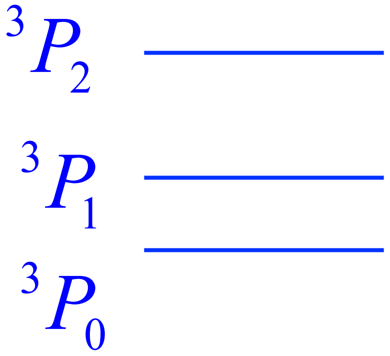
A rule for the energy interval btw out levels

- For a triplet,the E difference of the nearest levels is proportional to the larger J

- **E.g**

$^3P_{0,1,2}$

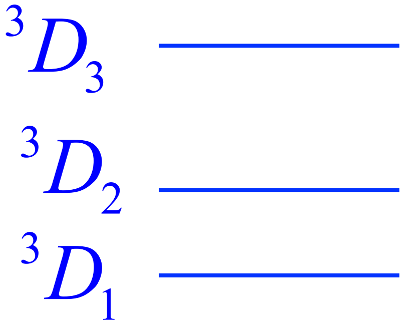
$$\frac{\varepsilon(^3P_2,{}^3P_1)}{\varepsilon(^3P_1,{}^3P_0)}=\frac{2}{1}$$



- **E.g**

$^3D_{1,2,3}$

$$\frac{\varepsilon(^3D_3,{}^3D_2)}{\varepsilon(^3D_2,{}^3D_1)}=\frac{3}{2}$$



Understand the landes rule

SL coupling→triplet splitting

$$\Delta E_{L\cdot S} \sim \vec{\mu}\cdot\vec{B} \sim \hat{S}\hat{L}\cos(\vec{L},\vec{S}) \sim \hat{S}\hat{L}\,\frac{\hat{J}^2-\hat{L}^2-\hat{S}^2}{2\hat{S}\hat{L}}$$

$$\sim J(J+1)-L(L+1)-S(S+1)$$

Energy gap btw J+1, J levels

$$(J+1)(J+2)-L(L+1)-S(S+1)$$

$$-[(J)(J+1)-L(L+1)-S(S+1)]$$

$$=(J+1)(J+2)-(J)(J+1)$$

$$=2(J+1)$$

5.4.5 Explanation for the variation of the ionization energies

- H, He, Li , Be, B, C, N, O,
- Na, Ar