Chap 8

Atomic physics

- Periodic table and exclusion principle
- Total angular momentum
- Spin-orbit coupling
- Hund’s rule
- Anomalous Zeeman effect

Periodic table (1869, Mendeleev)

Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

- Arranged by chemical properties and atomic weights (the atomic numbers are later determined from Mosley's experiment)
- The table is not complete. Based on the empty slots Mendeleev predicted three unknown elements, which was found later (Ga, Sc, Ge)

The Incredible Discovery of the LEAST Reactive Elements (The Noble Gases)

Modern periodic table

$1s^1$

hydrogen gas

period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

https://www.britannica.com/science/periodic-table

The periodic table can be understood by 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).

1923, Pauli extended Bohr's scheme to use four quantum numbers

(the nature of this m_s was not understood then).

Pauli exclusion principle: No two electrons in an atom may have the same set of quantum numbers (n, ℓ, m_ℓ, m_s).

The is valid for all particles with half-integer spin (called fermions).

(Later the spin-statistics theorem is derived by Pauli in 1940.)

- Hydrogen: $(n, \ell, m_\ell, m_s) = (1, 0, 0, \pm½)$, one *e* in ground state
- Helium: (1, 0, 0, ½) for the first electron

  (1, 0, 0, −½) for the second electron

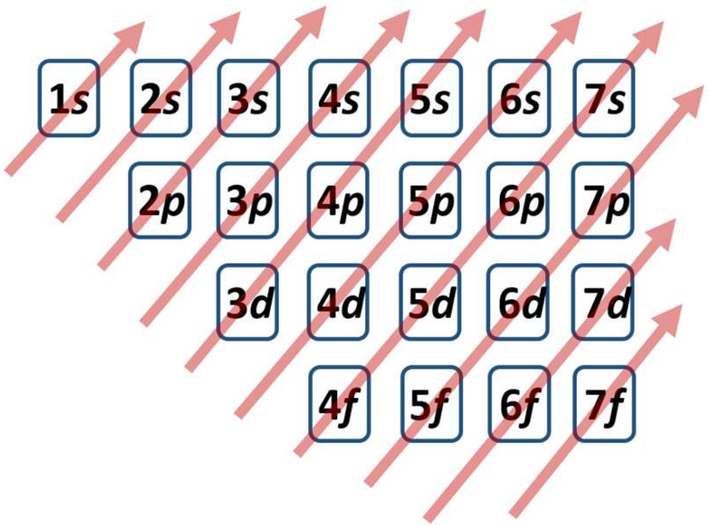
How many electrons may be in each subshell?

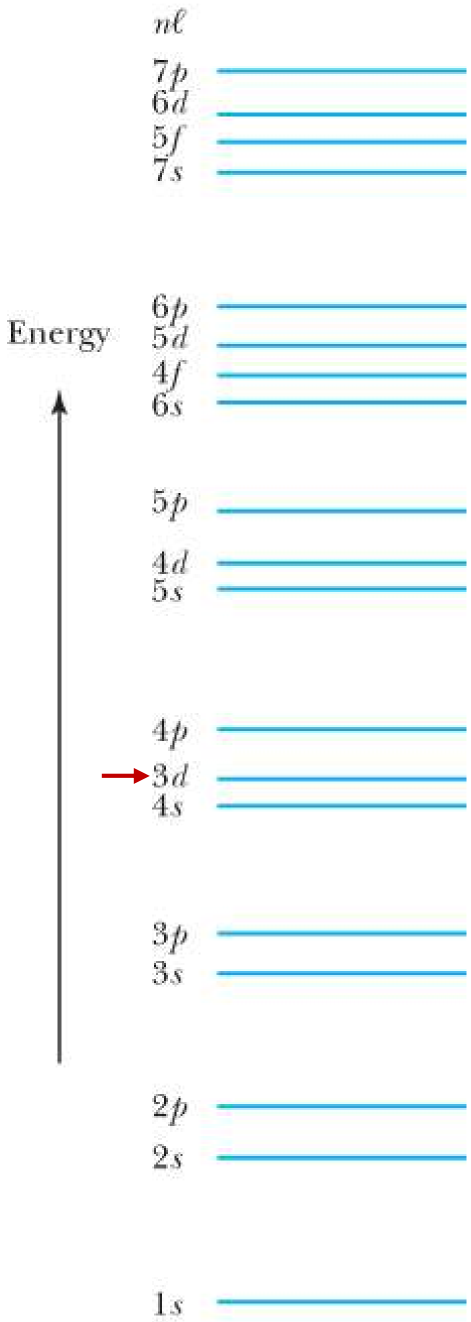
	Total
For each m_ℓ: two values of m_s	2
For each ℓ: $(2\ell + 1)$ values of m_ℓ	$2(2\ell + 1)$

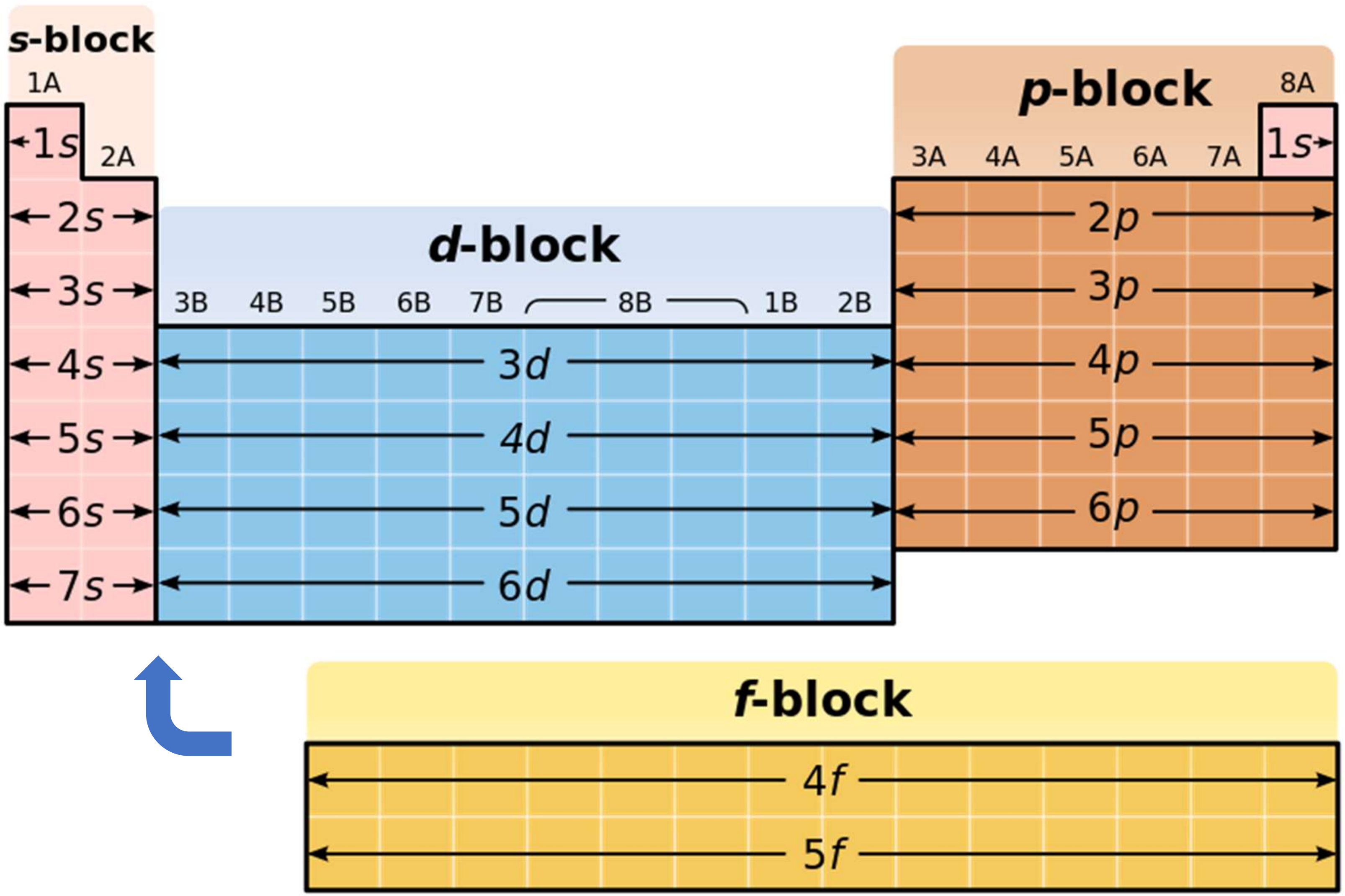
$\ell = 0$, (*s* state) can have two electrons

$\ell = 1$, (*p* state) can have six electrons, and so on

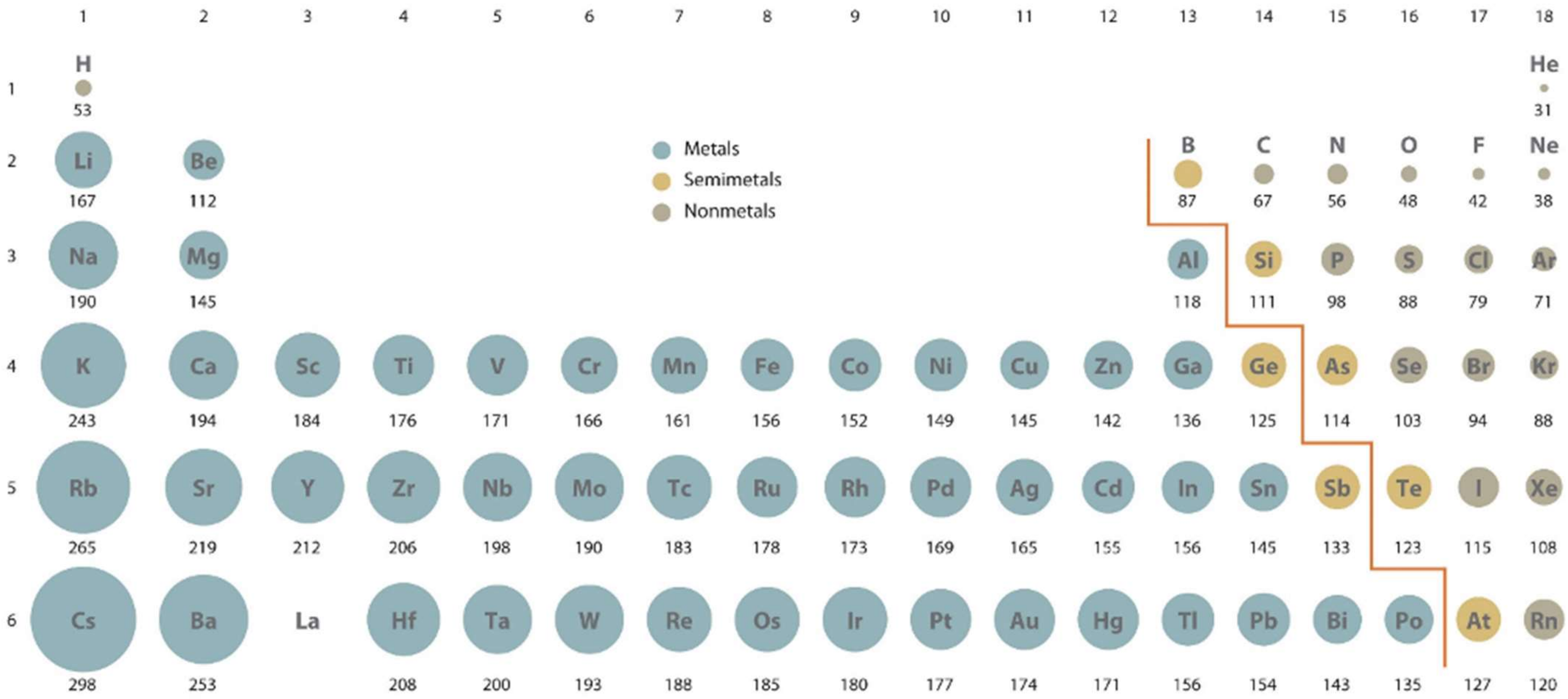
- Electrons with higher ℓ values are more shielded from the nuclear charge. They have higher energy than those with lower ℓ values
- E.g., 4*s* fills before 3d even though it has a larger *n*






s-block
1A
2A
1s
2s
3s
4s
5s
6s
7s
d-block
3B
4B
5B
6B
7B
8B
1B
2B
3d
4d
5d
6d
p-block
8A
3A
4A
5A
6A
7A
1s
2p
3p
4p
5p
6p
f-block
4f
5f

Atomic Radii



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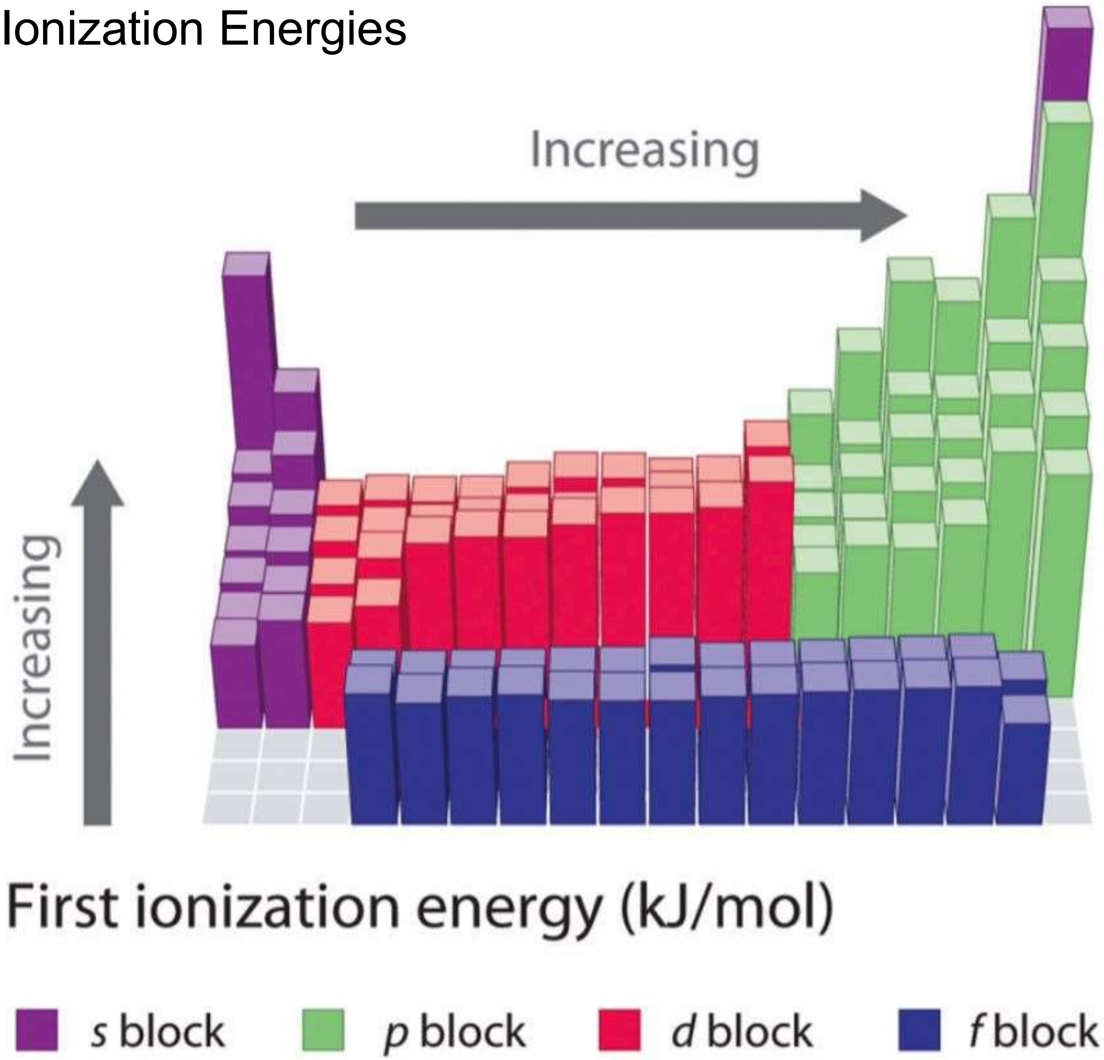
Ionization Energies



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In order to understand the spectra of atoms beyond the H atom, we need to have a deeper understanding of the angular momentum in quantum mechanics. The rules stated below could be deduced later in graduate-level course.

In the following, we discuss atoms with

- One electron (with spin)
- One electron (with spin) in B field
- Multiple electrons
- Multiple electrons in B field

Addition of angular momenta (see any textbook on QM):

Classical

Suppose there are 2 subsystems with angular momenta $\boldsymbol{J}_1$, $\boldsymbol{J}_2$,

then the total angular momentum $\boldsymbol{J}=\boldsymbol{J}_1+\boldsymbol{J}_2$

Quantum

- Subsystem 1

$\hat{\boldsymbol{J}}_1, \hat{J}_{1z}$

$$\hat{J}_1^2\psi_{j_1m_1} = j_1(j_1+1)\hbar^2\psi_{j_1m_1}$$

$$\hat{J}_{1z}\psi_{j_1m_1} = m_1\hbar\,\psi_{j_1m_1} \qquad m_1 = j_1, j_1-1, \cdots, -j_1$$

- Subsystem 2

$\hat{\boldsymbol{J}}_2, \hat{J}_{2z}$

$$\hat{J}_2^2\psi_{j_2m_2} = j_2(j_2+1)\hbar^2\psi_{j_2m_2}$$

$$\hat{J}_{2z}\psi_{j_2m_2} = m_2\hbar\,\psi_{j_2m_2} \qquad m_2 = j_2, j_2-1, \cdots, -j_2$$

- Composite system

$$\psi_{j_1j_2\,m_1m_2}$$

Alternative choice of quantum numbers $\psi_{j_1 j_2\, jm}$

- Operators

$$\begin{cases} \hat{\boldsymbol{J}} = \hat{\boldsymbol{J}}_1 + \hat{\boldsymbol{J}}_2 \\ \hat{J}_z = \hat{J}_{z1} + \hat{J}_{z2} \end{cases}$$

- Eigenstates

$$\begin{cases} \hat{\boldsymbol{J}}^2 \psi_{jm} = j(j+1)\hbar^2 \psi_{jm} \\ \hat{J}_z \psi_{jm} = m\hbar\, \psi_{jm} \end{cases}$$

$J = \sqrt{j(j+1)}\hbar$

$J_z = m_j \hbar$ magnitude

- Quantum numbers

Suppose 2 subsystems have quantum numbers j_1, j_2 ($j_1 > j_2$),

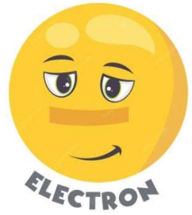
then for the combined system, the quantum number j can be

$$j = j_1 + j_2, j_1 + j_2 - 1, \cdots, j_1 - j_2$$

For a given j, $m = j, j-1, \cdots, -j$

Also $m = m_1 + m_2$

e.g., $j_1 = 1, j_2 = 1$



An atom with only one electron (with spin)

Orbital and spin angular momenta,

$$\begin{cases} \mathbf{J} = \mathbf{L} + \mathbf{S} \\ J_z = L_z + S_z \end{cases}$$

$\mathbf{J}_1 = \mathbf{L}$, $\mathbf{J}_2 = \mathbf{S}$

$j_1 = \ell, j_2 = \frac{1}{2}$

For total angular momentum, the quantum number j can have the values

$$j = \ell \pm s = \ell \pm 1/2$$

$$j = j_1 + j_2, j_1 + j_2 - 1, \cdots, j_1 - j_2$$

$$m = j, j-1, \cdots, -j$$

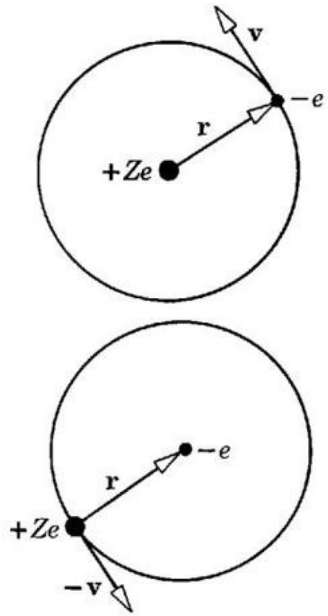
Also, $m = m_\ell + m_s$

$$m = m_1 + m_2$$

Example 8-5. Enumerate the possible values of the quantum numbers j and m_j, for states in which $l = 2$ and, of course, $s = 1/2$.

►According to (8-33a), the two possible values of j are 5/2 and 3/2. According to (8-31), for $j = 5/2$ the possible values of m_j are $-5/2$, $-3/2$, $-1/2$, $1/2$, $3/2$, $5/2$. The same equation states that for $j = 3/2$ the possible values of m_j are $-3/2$, $-1/2$, $1/2$, $3/2$.

Spin-orbit coupling (SOC)



- An electron is like a small magnet, due to spin
- In electron's frame, it feels an effective magnetic field due to the circulating nucleus

$$\mathbf{E} = \frac{Ze}{4\pi\epsilon_0}\frac{\mathbf{r}}{r^3}$$

Biot-Savart law ➡ $$\mathbf{B} = \frac{\mu_0}{4\pi}\frac{\mathbf{j}\times\mathbf{r}}{r^3} = -\frac{Ze\mu_0}{4\pi}\frac{\mathbf{v}\times\mathbf{r}}{r^3}$$ ➡ $$\mathbf{B} = -\frac{1}{c^2}\mathbf{v}\times\mathbf{E}$$

Zeeman coupling energy $\Delta E = -\boldsymbol{\mu}_s \cdot \mathbf{B}$

$$\begin{aligned}
H_{SO} &= -\vec{\mu}\cdot\vec{B}_{eff} \\
&= +\left(\frac{e}{m}\vec{S}\right)\cdot\left(\vec{E}\times\frac{\vec{v}}{c^2}\right), \quad \vec{E} = -\hat{r}\frac{d\phi}{dr}. \ \text{For H atom, } \phi = +\frac{e}{4\pi\varepsilon_0 r}. \\
&= \left(\frac{-e}{m^2c^2}\frac{d\phi}{rdr}\right)\vec{S}\cdot\vec{L} \\
&\equiv f(r)\vec{S}\cdot\vec{L}
\end{aligned}$$

Note: Thomas precession $(\times\ \frac{1}{2})$

optional

- For the n=2, l=1 state of the H atom, estimate the magnitude of the SO coupling energy

Eisberg and Resnick, Chap 8

$$V = -e\phi \qquad V(r) = -\frac{e^2}{4\pi\epsilon_0} r^{-1} \qquad \frac{dV(r)}{dr} = \frac{e^2}{4\pi\epsilon_0} r^{-2}$$

$$\Delta E = \frac{e^2}{4\pi\epsilon_0 2m^2c^2} \frac{1}{r^3} \mathbf{S} \cdot \mathbf{L}$$

$$\left\langle \frac{1}{r^3} \right\rangle_{n=2} = \frac{1}{(3a_0)^3}, \qquad \vec{S} \cdot \vec{L} \simeq \hbar^2$$

$$\Rightarrow \quad |\Delta E| \sim 10^{-4}\ \text{eV}$$

The splitting of spectral lines due to the SOC is called the fine structure of the spectrum 精細結構

- Estimate the magnetic field that gives the same amount of splitting

$$|\Delta E| \sim \mu_s B$$

$$\mu_s \simeq \mu_b = 0.058\ \text{meV/T}$$

$$\Rightarrow \quad B \simeq 1\ \text{T}$$

optional

- For the case above, there are many quantities related to the angular momentum: $L^2, L_z, S^2, S_z, J^2, J_z$

  These give six quantum numbers $(\ell, m_\ell, s, m_s, j, m_j)$
- Q: How do we use them to label energy eigenstates?

  A: Find physical observables that can commute with *H*, and also commute with each other. They have simultaneous energy eigenstates, and the eigenenergy *E* can be labeled by their quantum numbers (called good quantum numbers).
- For example, $H = H_0 + f(\vec{r})\vec{L}\cdot\vec{S}, \quad H_0 = \dfrac{p^2}{2m} + V(r)$

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \qquad \mathbf{J}\cdot\mathbf{J} = \mathbf{L}\cdot\mathbf{L} + \mathbf{S}\cdot\mathbf{S} + 2\,\mathbf{S}\cdot\mathbf{L}$$

➡ $\mathbf{S}\cdot\mathbf{L} = (J^2 - L^2 - S^2)/2$

So H commute with $L^2, S^2, J^2,$ and J_z (but not L_z, S_z).

➡ $(\ell, m_\ell, s, m_s, j, m_j)$

- (H, L^2, S^2, J^2, J_z) mutually commute with each other.

So (ℓ, s, j, m_j) are good quantum numbers that can label eigenenergy *E*.

$$j = \ell \pm s = \ell \pm 1/2$$

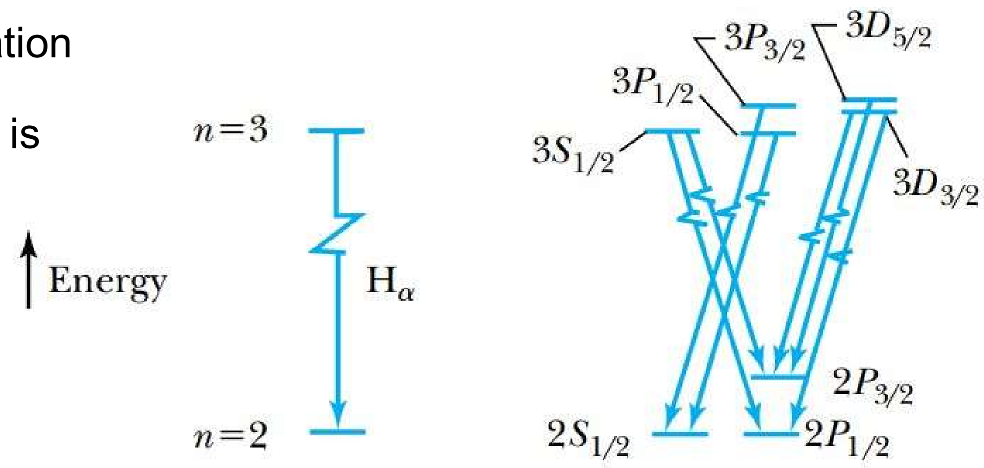
- Consider an energy eigenstate ψ_{n,ℓ,s,j,m_j}

$$H\psi_{n,\ell,s,j,m_j} = E_{n,\ell,s,j,m_j}\psi_{n,\ell,s,j,m_j}$$

$$\Rightarrow \quad \vec{L} \cdot \vec{S}\psi_{n,\ell,s,j,m_j} = \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\psi_{n,\ell,s,j,m_j}$$

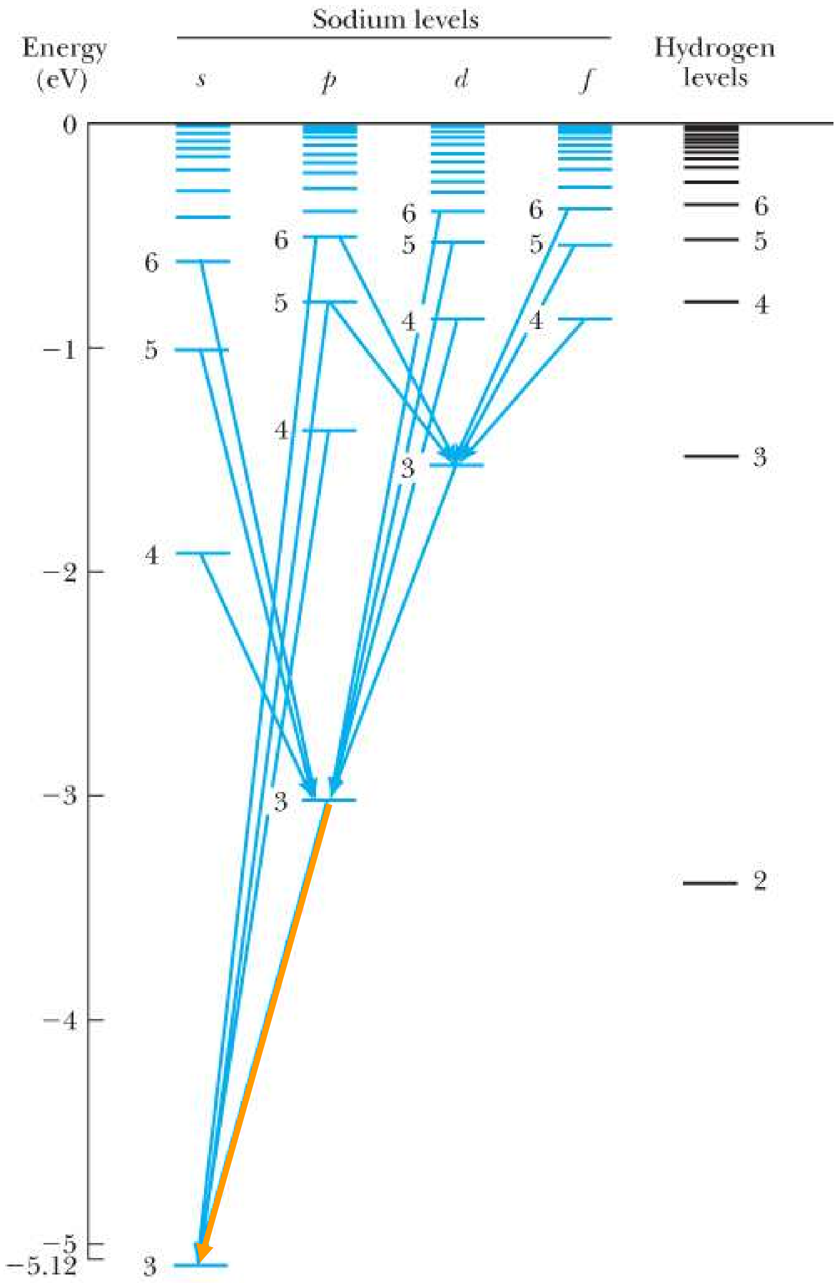
- Spectroscopic notation

The state ψ_{n,ℓ,s,j,m_j} is written as nL_j.



Without SOC With SOC

Energy-Level Diagram of Sodium



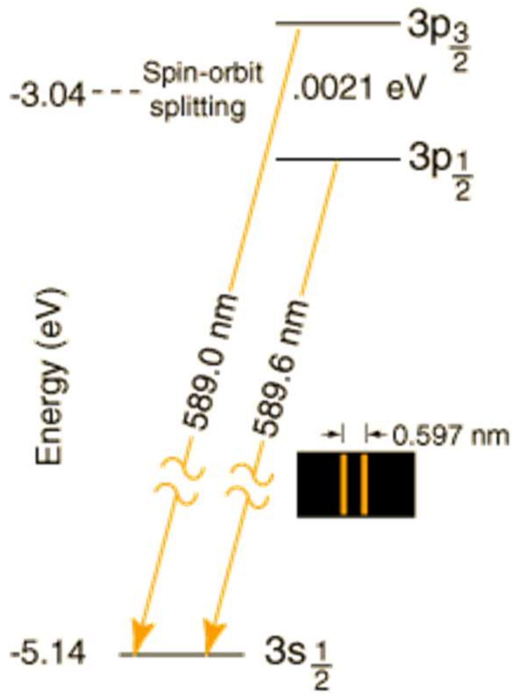
- Several transitions are missing. This leads to the selection rule:

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

(j=0 to j=0 is forbidden)

$$\Delta \ell = \pm 1$$

- The transitions that generate the doublet

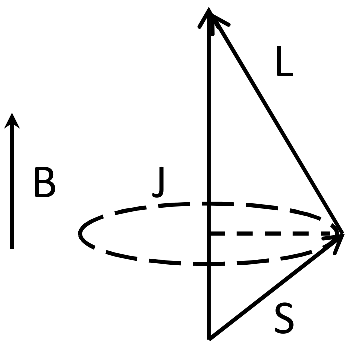


Sodium doublet

$\boxed{\vec{B} \neq 0}$ Anomalous Zeeman effect (spin + SOC + B field)

$$\vec{\mu} = -\frac{e}{2m}\left(\vec{L} + 2\vec{S}\right)$$

- Heuristic argument: ***J*** is fixed, ***L*** and ***S*** rotate around ***J***, maintaining the triangle. So the magnetic moment is given by the component of ***L***+2***S*** = ***J***+***S*** parallel to ***J***,



$$\vec{S}_{//} = (\vec{S}\cdot\hat{J})\hat{J} = \frac{\vec{J}}{2J^2}\left(J^2 - L^2 + S^2\right)$$

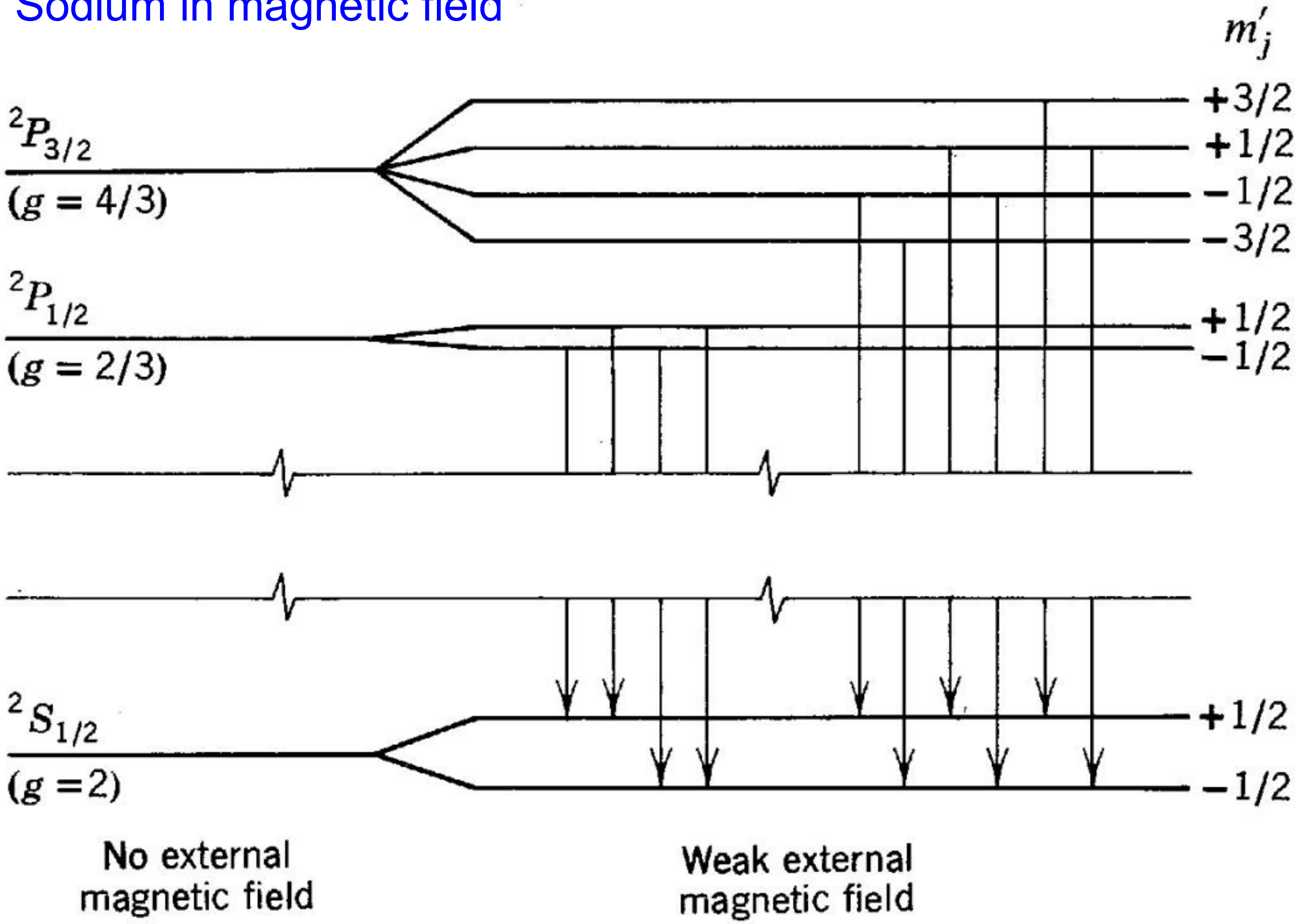
magnitude ➡ $\frac{\vec{J}}{2J(J+1)}\left[J(J+1) - L(L+1) + S(S+1)\right]$

$$\therefore \vec{\mu}_{eff} = -\frac{e}{2m}\left(\vec{J} + \vec{S}_{//}\right) = -g_J \frac{e}{2m}\vec{J}$$

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$ Lande *g*-factor (1921)

➡ $\Delta E_{m_j} = -\vec{\mu}_{eff}\cdot\vec{B} = g_J \mu_B m_j, \qquad \mu_B \equiv \frac{e\hbar}{2m}$

Sodium in magnetic field



Selection rules

$\Delta j = 0, \pm 1$ (j=0 to j=0 is forbidden)

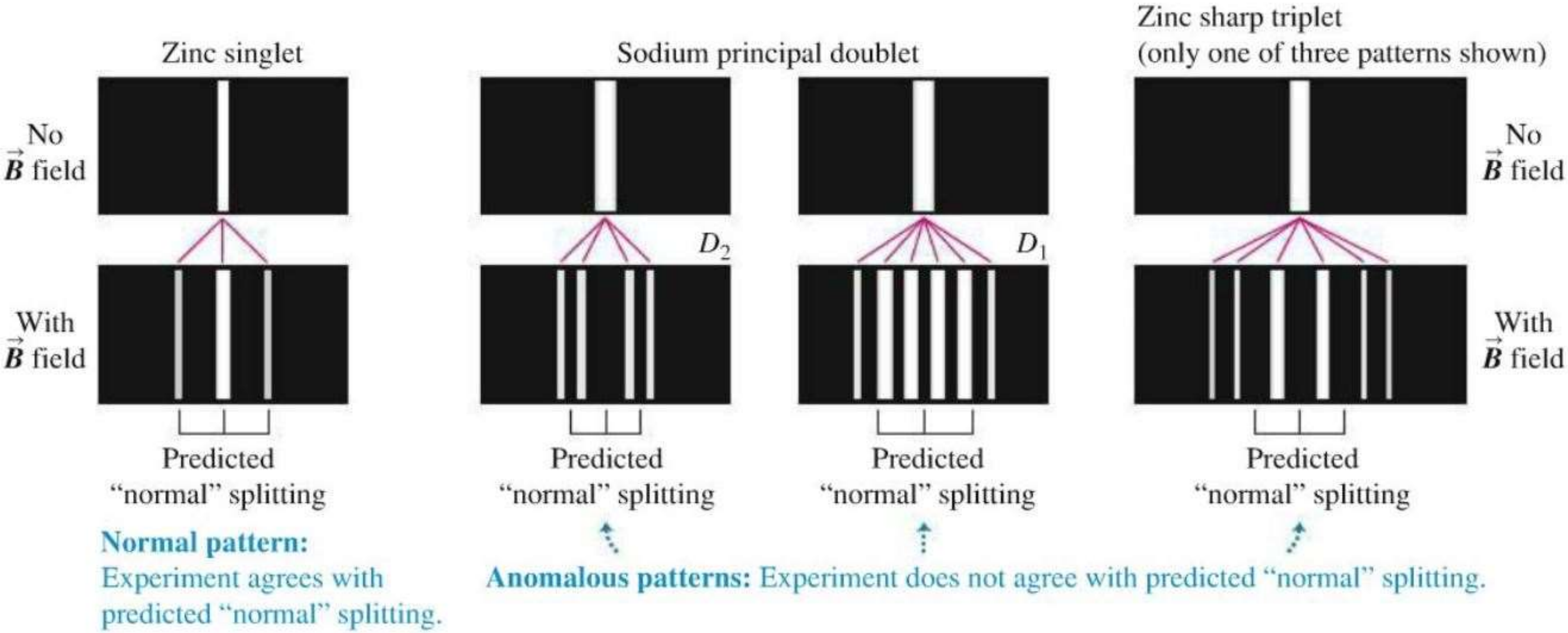
$\Delta \ell = \pm 1$, $\Delta s = 0$

$\Delta m_j = 0, \pm 1$ (in $\boldsymbol{B}$ field)

Eisberg and Resnick, Chap 10

no spin

spin + spin-orbit coupling



- The energy of an atom with one electron depends on (n, ℓ) →

- The energy of an atom with many electrons

$$H = \sum_i \left(\frac{p_i^2}{2m} + V_i \right) + \frac{1}{2} \sum_{ij} V_{ij} + \sum_i \lambda_i \vec{S}_i \cdot \vec{L}_i$$

Compatible operators

$$H, L^2, S^2, J^2, J_z \quad \Rightarrow \quad (n, L, S, J, m_J)$$

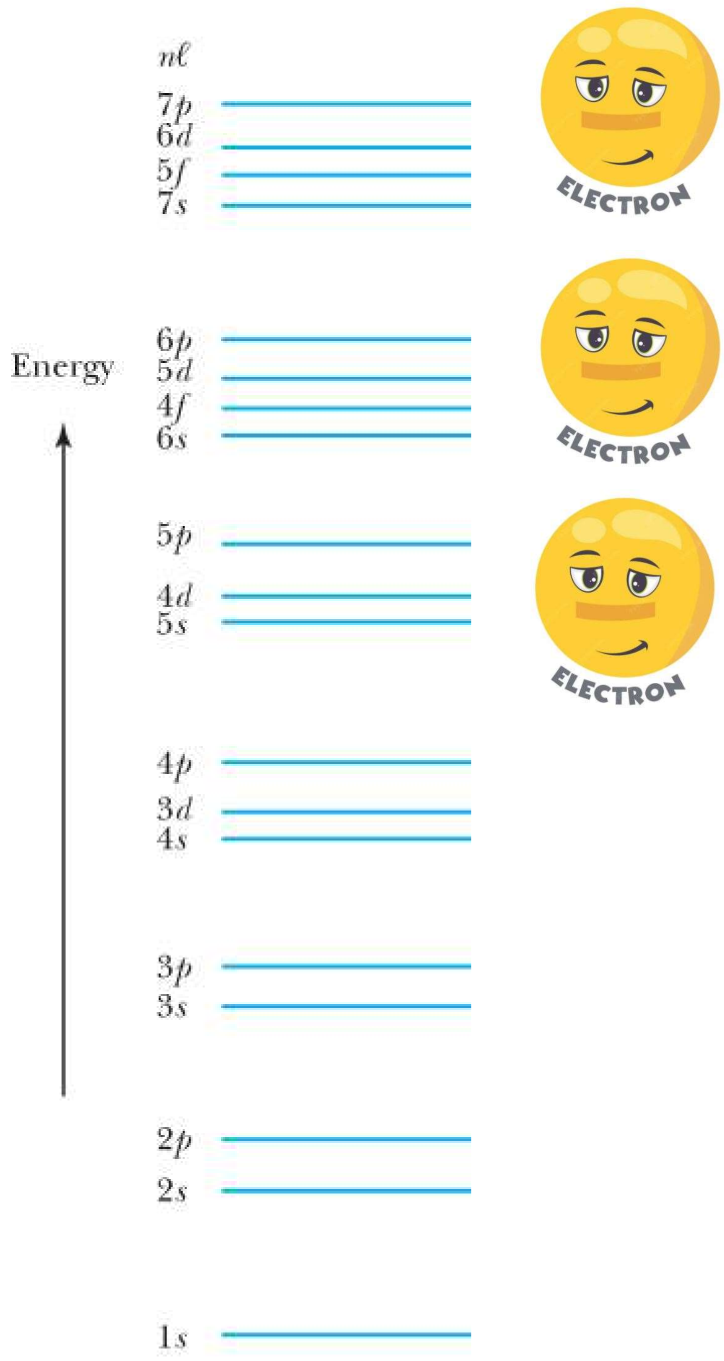
explicit only in B field

Without ***B***, the energy depends on (n, L, S, J)

- Spectroscopic notation $\boxed{n^{2S+1}L_J}$

For L>S, given a L, there are 2*S*+1 values of J (from L+S to L-S), and 2S+1 is the **multiplicity** of the state.

For L<S, the multiplicity is less than 2S+1.



Due to e-e interaction, states with different (*L,S,J*) have different energies.

Which one has the lowest energy? That is,

What's the values of *L*, *S*, and *J* for the atomic ground state?

Hund's rules (1925): 洪德法則

1. Choose the max value of *S* that is consistent with the exclusion principle
2. Choose the max value of *L* that is consistent with the exclusion principle and the 1st rule
3. If less than half-filled, then $J=|L-S|$ has the lowest energy

   If more than half-filled, then $J=L+S$ has the lowest energy

To reduce Coulomb repulsion, electron spins like to be parallel, electron orbital motion likes to be in high m_l state. Both help disperse the charge distribution.

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	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓

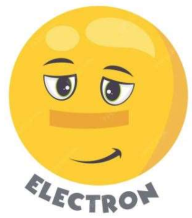
According to Hund's rules

d-shell ($l = 2$)									
n	$l_z = 2,$	$1,$	$0,$	$-1,$	-2	S	$L = \lvert\Sigma l_z\rvert$	J	SYMBOL
1	↓					1/2	2	3/2	$^2D_{3/2}$
2	↓	↓				1	3	2	$^3F_2$
3	↓	↓	↓			3/2	3	3/2	$^4F_{3/2}$
4	↓	↓	↓	↓		2	2	0	$^5D_0$
5	↓	↓	↓	↓	↓	5/2	0	5/2	$^6S_{5/2}$
6	⇅	↑	↑	↑	↑	2	2	4	$^5D_4$
7	⇅	⇅	↑	↑	↑	3/2	3	9/2	$^4F_{9/2}$
8	⇅	⇅	⇅	↑	↑	1	3	4	$^3F_4$
9	⇅	⇅	⇅	⇅	↑	1/2	2	5/2	$^2D_{5/2}$
10	⇅	⇅	⇅	⇅	⇅	0	0	0	$^1S_0$

$J = |L - S|$ (n = 1–4)

$J = L + S$ (n = 6–9)

Qubear 原子磁性：懂薛丁格方程式也要懂宏德法則



Two valence electrons, e.g., 4p+4d

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

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

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

L_1=1

L_2=2

S_1=1/2

S_2=1/2

L=3,2,1

S=1,0

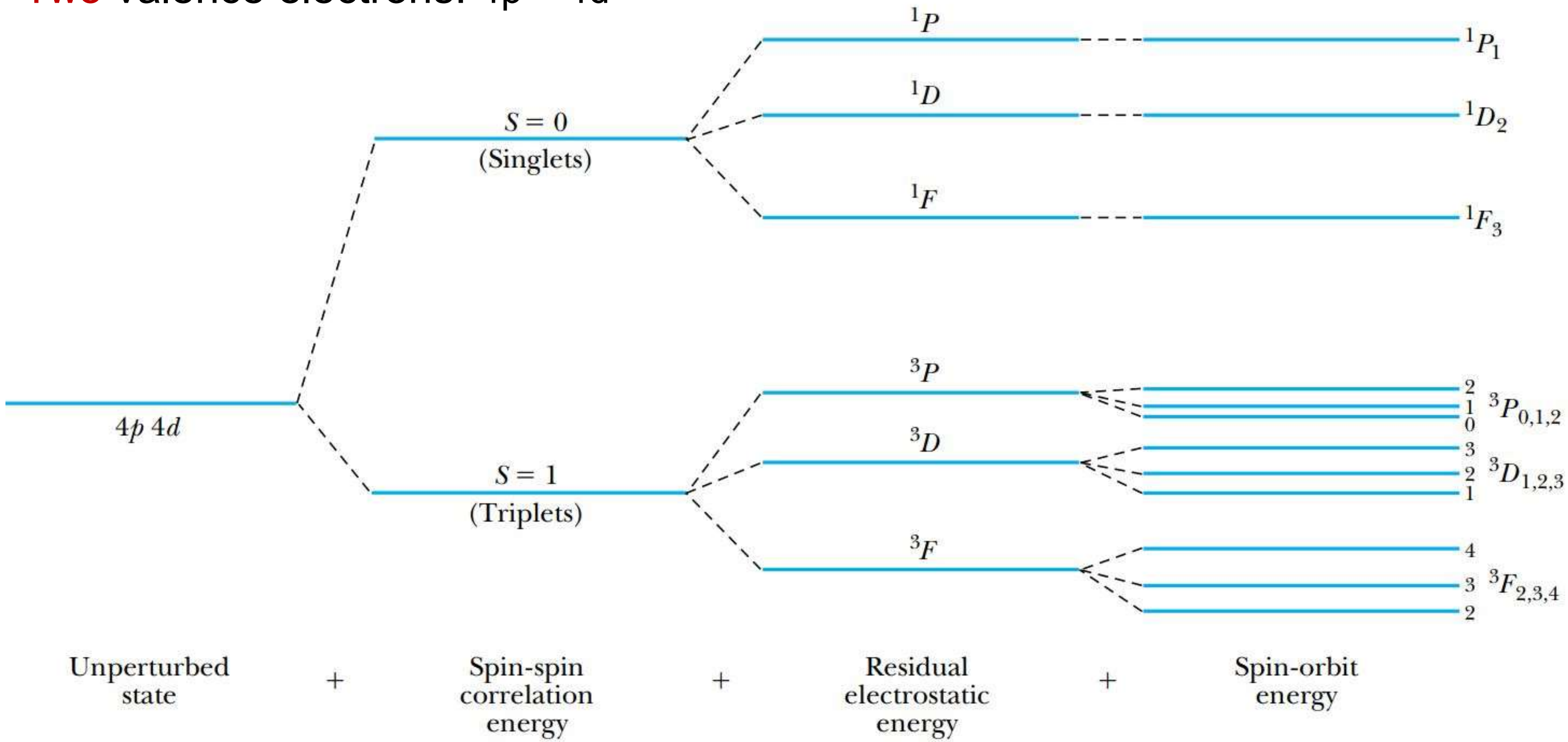
J=L+S … |L-S|

Table 8.2 Spectroscopic Symbols for Two Electrons: One in 4*p* and One in 4*d*

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

Hund's rule only tell you that the ground state is $4\ {}^3F_2$

Two valence electrons: 4p + 4d



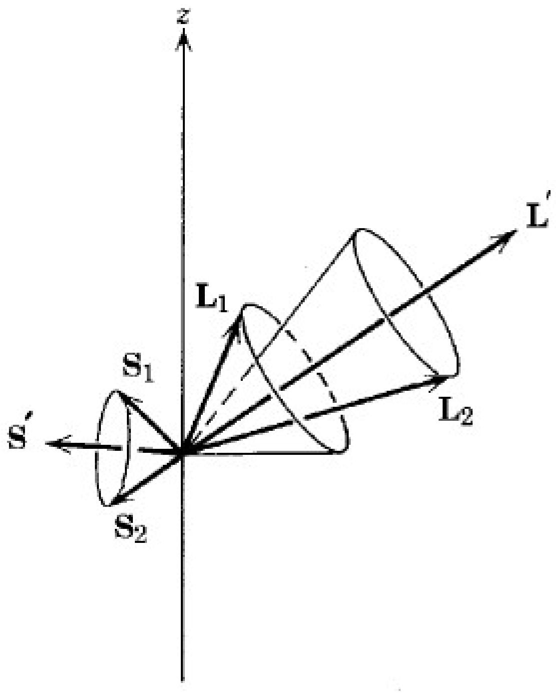
Two types of angular momentum coupling

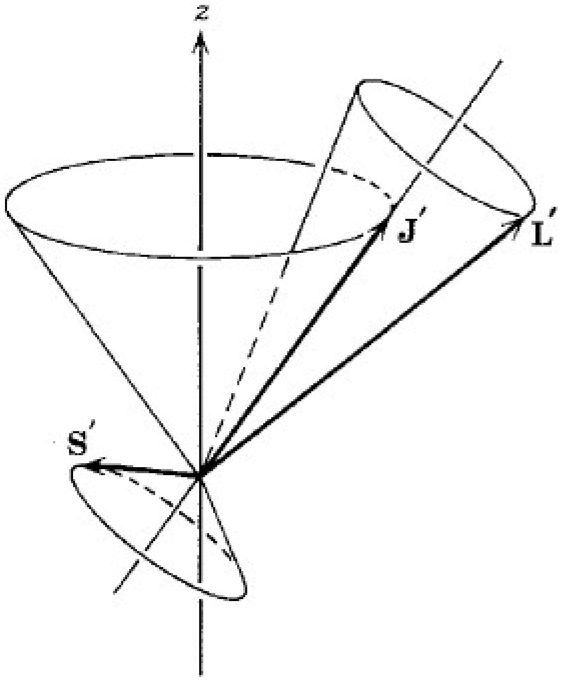
- LS coupling
  Light atoms (Z<30)

$$\vec{L} = \vec{L}_1 + \vec{L}_2$$
$$\vec{S} = \vec{S}_1 + \vec{S}_2$$
$$\Rightarrow \quad \vec{J} = \vec{L} + \vec{S}$$

- JJ coupling
  Heavy atoms

$$\vec{J}_1 = \vec{L}_1 + \vec{S}_1$$
$$\vec{J}_2 = \vec{L}_2 + \vec{S}_2$$
$$\Rightarrow \quad \vec{J} = \vec{J}_1 + \vec{J}_2$$





Ex 8.4:

What are the total angular momentum and the spectroscopic notation for the ground state of helium?

Solution The two electrons for helium are both 1*s* electrons. Because helium is a light atom, we use the *LS* coupling scheme. We have $L_1 = 0$ and $L_2 = 0$, and therefore $L = 0$. We can have $S = 0$ or 1 for two electrons, but not in the same subshell. The spins must be antialigned and $S = 0$. Therefore $J = 0$ also. We can write the ground-state spectroscopic symbol for helium as 1^1S_0.

Ex 8.5:

Consider two electrons in an atom with orbital quantum numbers $\ell_1 = 1$ and $\ell_2 = 2$. Use *LS* coupling and find all possible values for the total angular momentum quantum numbers for $\vec{J}$.

Solution First, total spin angular momentum, S = 0 or 1.

Second, total orbital angular momentum quantum number ranges from $|\ell_1 - \ell_2|$ to $|\ell_1 + \ell_2|$, so we have values of L =1, 2, and 3.

Now $\vec{J} = \vec{L} + \vec{S}$ and the range of quantum numbers for J range from $|L - S|$ to $|L + S|$, so we have values of $J = 0, 1, 2, 3, 4$.

Ex 8.7: What are the L, S, and J values for the first few excited states of helium?

Solution The possibilities are

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

$$\text{If } S = 0, \text{ then } J = 0$$

$$\text{If } S = 1, \text{ then } J = 1$$

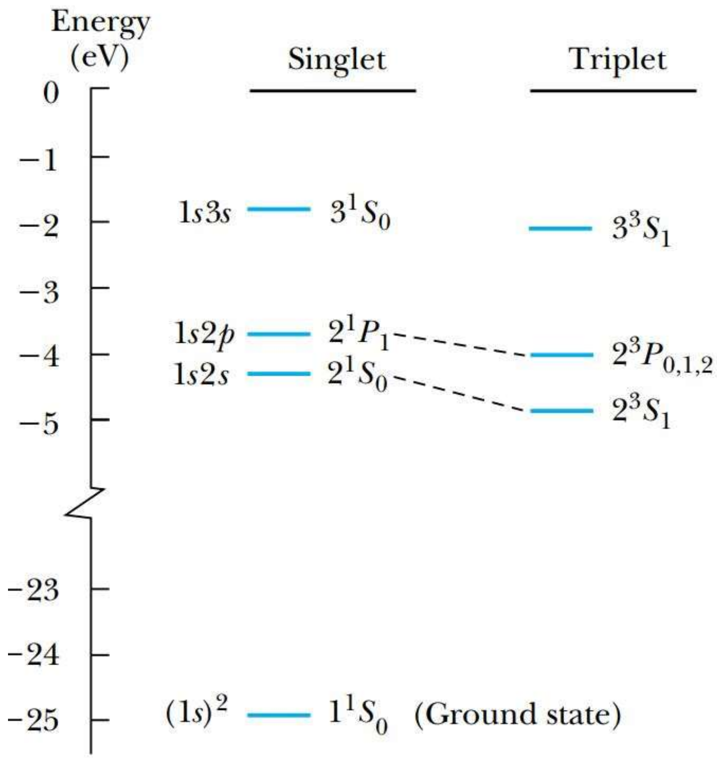
with $S = 1$ being lowest in energy. The lowest excited state is ${}^3S_1$ and then comes ${}^1S_0$.

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

$$\text{If } S = 0, \text{ then } J = 1$$

$$\text{If } S = 1, \text{ then } J = 0, 1, 2$$

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.



Ex 8.9: What are the possible energy states for atomic carbon?

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

Example 10-5. Evaluate the Landé g factor for the $^3P_1$ level in the $2p3s$ configuration of the ^{6}C atom, and use the result to predict the splitting of the level when the atom is in an external magnetic field of 0.1 tesla.

▶ For the $^3P_1$ state $s' = l' = j' = 1$. So

$$g = 1 + \frac{1(1+1) + 1(1+1) - 1(1+1)}{2 \times 1(1+1)} = 1 + \frac{2}{2 \times 2} = \frac{3}{2}$$

For $j' = 1$ the possible values of m_j' are $-1, 0, 1$, so the level is split into three components, one with the same energy and the others displaced in energy by

$$\begin{aligned} \Delta E = \mu_b B g m_j' &= \pm \mu_b B g = \pm 9.3 \times 10^{-24}\ \text{amp-m}^2 \times 10^{-1}\ \text{tesla} \times 1.5 \\ &= \pm 1.4 \times 10^{-24}\ \text{joule} \\ &= \pm 8.7 \times 10^{-6}\ \text{eV} \end{aligned}$$

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Eisberg and Resnick, Chap 10