The LS-coupling scheme

Atomic Physics Chapter 5

LHRG李

School of Physics, Peking University

July 2024

5.0 Hamiltonian&The LS-coupling scheme without fine structure

Hamiltonian

The central-field approximation

$$V_{\text{CF}}(r) = -\frac{Ze^2/4\pi\epsilon_0}{r} + S(r),$$

$$H_{\text{CF}} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{CF}}(r_i) \right\}.$$

The residual electrostatic interaction:

$$H_{\text{re}} = \sum_{i=1}^{N} \left\{ \sum_{j>i}^{N} \frac{e^2/4\pi\epsilon_0}{r_{ij}} - S(r_i) \right\},$$

Hamiltonian:

$$H = H_{\text{CF}} + H_{\text{re}} + H_{\text{s-o}}.$$

Hamiltonian

The central-field approximation

$$V_{\text{CF}}(r) = -\frac{Ze^2/4\pi\epsilon_0}{r} + S(r),$$

$$H_{\text{CF}} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{CF}}(r_i) \right\}.$$

The residual electrostatic interaction:

$$H_{\text{re}} = \sum_{i=1}^{N} \left\{ \sum_{j>i}^{N} \frac{e^2/4\pi\epsilon_0}{r_{ij}} - S(r_i) \right\},$$

Hamiltonian:

$$H = H_{\text{CF}} + H_{\text{re}} + H_{\text{s-o}}.$$

Hamiltonian

The central-field approximation

$$V_{\text{CF}}\left(r\right) = -\frac{Ze^2/4\pi\epsilon_0}{r} + S(r),$$

$$H_{\text{CF}} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{CF}}\left(r_i\right) \right\}.$$

The residual electrostatic interaction:

$$H_{\text{re}} = \sum_{i=1}^{N} \left\{ \sum_{j>i}^{N} \frac{e^2/4\pi\epsilon_0}{r_{ij}} - S(r_i) \right\},$$

Hamiltonian:

$$H = H_{\text{CF}} + H_{\text{re}} + H_{\text{s-o}}.$$

Hamiltonian

It is generally very difficult to calculate the eigenvalues of the above Hamiltonian, so two extremes are usually discussed.

1. LS-coupling scheme:

   $H_{s-o} \ll H_{re} : H_{s-o} \rightarrow$ perturbation, basic quantum numbers : $LSJM_J$,

2. jj-coupling scheme:

   $H_{s-o} \gg H_{re} : H_{re} \rightarrow$ perturbation, basic quantum numbers : $n_i l_i j_i J M_J$.

It is generally very difficult to calculate the eigenvalues of the above Hamiltonian, so two extremes are usually discussed.

1. LS-coupling scheme:

$$H_{s-o} \ll H_{re} : H_{s-o} \rightarrow \text{perturbation, basic quantum numbers} : LSJM_J,$$

2. jj-coupling scheme:

$$H_{s-o} \gg H_{re} : H_{re} \rightarrow \text{perturbation, basic quantum numbers} : n_i l_i j_i J M_J.$$

It is generally very difficult to calculate the eigenvalues of the above Hamiltonian, so two extremes are usually discussed.

1. LS-coupling scheme:

    $H_{\text{s}-\text{o}} \ll H_{\text{re}} : H_{\text{s}-\text{o}} \rightarrow$ perturbation, basic quantum numbers : $LSJM_J$,

2. jj-coupling scheme:

    $H_{\text{s}-\text{o}} \gg H_{\text{re}} : H_{\text{re}} \rightarrow$ perturbation, basic quantum numbers : $n_i l_i j_i J M_J$.

LS-coupling scheme without fine structure

Hamiltonian

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{CF}}(r_i) + \left\{ \sum_{j>i}^{N} \frac{e^2/4\pi\epsilon_0}{r_{ij}} - S(r_i) \right\} \right],$$

$$H = H_{\text{CF}} + H_{\text{re}}.$$

Consider

$$\boldsymbol{L} = \sum_i l_i, \quad \boldsymbol{S} = \sum_i s_i, \quad \boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}.$$

No external torque:

$$\left[\boldsymbol{L}^2, H_{\text{re}}\right] = 0 \quad \text{and} \quad [L_z, H_{\text{re}}] = 0.$$

H_{re} doesn't depend on spin:

$$\left[\boldsymbol{S}^2, H_{\text{re}}\right] = 0 \quad \text{and} \quad [S_z, H_{\text{re}}] = 0.$$

LS-coupling scheme without fine structure

Hamiltonian

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\mathrm{CF}}(r_i) + \left\{ \sum_{j>i}^{N} \frac{e^2/4\pi\epsilon_0}{r_{ij}} - S(r_i) \right\} \right],$$

$$H = H_{\mathrm{CF}} + H_{\mathrm{re}}.$$

Consider

$$\boldsymbol{L} = \sum_i \boldsymbol{l}_i, \quad \boldsymbol{S} = \sum_i \boldsymbol{s}_i, \quad \boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}.$$

No external torque:

$$\left[\boldsymbol{L}^2, H_{\mathrm{re}} \right] = 0 \quad \text{and} \quad \left[L_z, H_{\mathrm{re}} \right] = 0.$$

H_{re} doesn't depend on spin:

$$\left[\boldsymbol{S}^2, H_{\mathrm{re}} \right] = 0 \quad \text{and} \quad \left[S_z, H_{\mathrm{re}} \right] = 0.$$

PEKING UNIVERSITY

Hamiltonian

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{CF}}(r_i) + \left\{ \sum_{j>i}^{N} \frac{e^2/4\pi\epsilon_0}{r_{ij}} - S(r_i) \right\} \right],$$

$$H = H_{\text{CF}} + H_{\text{re}}.$$

Consider

$$\boldsymbol{L} = \sum_i \boldsymbol{l}_i, \quad \boldsymbol{S} = \sum_i \boldsymbol{s}_i, \quad \boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}.$$

No external torque:

$$\left[\boldsymbol{L}^2, H_{\text{re}} \right] = 0 \quad \text{and} \quad [L_z, H_{\text{re}}] = 0.$$

H_{re} doesn't depend on spin:

$$\left[\boldsymbol{S}^2, H_{\text{re}} \right] = 0 \quad \text{and} \quad [S_z, H_{\text{re}}] = 0.$$

LS-coupling scheme without fine structure

Hamiltonian

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{CF}}(r_i) + \left\{ \sum_{j>i}^{N} \frac{e^2/4\pi\epsilon_0}{r_{ij}} - S(r_i) \right\} \right],$$

$$H = H_{\text{CF}} + H_{\text{re}}.$$

Consider

$$\boldsymbol{L} = \sum_i \boldsymbol{l}_i, \quad \boldsymbol{S} = \sum_i \boldsymbol{s}_i, \quad \boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}.$$

No external torque:

$$\left[\boldsymbol{L}^2, H_{\text{re}} \right] = 0 \quad \text{and} \quad [L_z, H_{\text{re}}] = 0.$$

H_{re} doesn't depend on spin:

$$\left[\boldsymbol{S}^2, H_{\text{re}} \right] = 0 \quad \text{and} \quad [S_z, H_{\text{re}}] = 0.$$

LS-coupling scheme without fine structure

Therefore,

$$\text{good quantum numbers}: L, M_L, S, M_S,$$
$$\text{eigenstates of} H_{\text{re}}: |LM_LSM_S\rangle.$$

Label:

$$\textbf{terms}: {}^{2S+1}L_J.$$

e.g. 3p4p in silicon

$$l_1 = 1, \quad l_2 = 1 \quad \Rightarrow \quad L = 0, 1 \text{ or } 2,$$
$$s_1 = \frac{1}{2}, \quad s_2 = \frac{1}{2} \quad \Rightarrow \quad S = 0 \text{ or } 1,$$
$$\text{terms (without J)}: \quad {}^{2S+1}L = {}^1\text{S}, {}^1\text{P}, {}^1\text{D}, {}^3\text{S}, {}^3\text{P}, {}^3\text{D}.$$

Therefore,

$$\text{good quantum numbers}: L, M_L, S, M_S,$$
$$\text{eigenstates of } H_{\text{re}}: |LM_LSM_S\rangle.$$

Label:

$$\textbf{terms}: {}^{2S+1}L_J.$$

e.g. 3p4p in silicon

$$l_1 = 1, \quad l_2 = 1 \quad \Rightarrow \quad L = 0, 1 \text{ or } 2,$$
$$s_1 = \frac{1}{2}, \quad s_2 = \frac{1}{2} \quad \Rightarrow \quad S = 0 \text{ or } 1,$$
$$\text{terms (without J)}: \quad {}^{2S+1}L = {}^1S, {}^1P, {}^1D, {}^3S, {}^3P, {}^3D.$$

Therefore,

$$\text{good quantum numbers}: L, M_L, S, M_S,$$
$$\text{eigenstates of} H_{\text{re}}: |LM_LSM_S\rangle.$$

Label:

$$\textbf{terms}: {}^{2S+1}L_J.$$

---

e.g. 3p4p in silicon

$$l_1 = 1, \quad l_2 = 1 \quad \Rightarrow \quad L = 0, 1 \text{ or } 2,$$
$$s_1 = \frac{1}{2}, \quad s_2 = \frac{1}{2} \quad \Rightarrow \quad S = 0 \text{ or } 1,$$

$$\text{terms (without J)}: \quad {}^{2S+1}L = {}^1\text{S}, {}^1\text{P}, {}^1\text{D}, {}^3\text{S}, {}^3\text{P}, {}^3\text{D}.$$

Energy levels

Isotropy: degeneracy with respect to M_L and M_S.

Figure: 3p4p in silicon

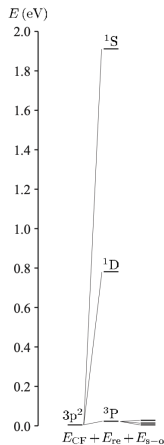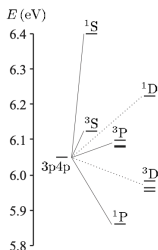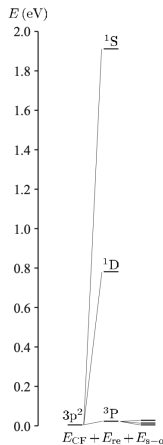Degenerate states

$(2l_1+1)(2l_2+1)(2s_1+1)(2s_2+1) = 36.$

Figure: $3p^2$ in silicon

Energy levels

Isotropy: degeneracy with respect to M_L and M_S.

Figure: 3p4p in silicon

Figure: $3p^2$ in silicon

Degenerate states

$$(2l_1+1)(2l_2+1)(2s_1+1)(2s_2+1) = 36.$$

Energy levels
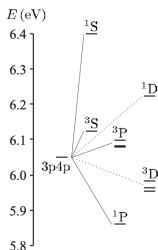
Isotropy: degeneracy with respect to M_L and M_S.

Figure: 3p4p in silicon

Figure: $3p^2$ in silicon

Degenerate states

$$(2l_1+1)(2l_2+1)(2s_1+1)(2s_2+1) = 36.$$

Content

北京大学
PEKING UNIVERSITY

Spin orbit coupling of electrons

Approximate calculations of relativistic quantum mechanics at low speeds:

$$U_{sl} = \frac{1}{2\mu^2 c^2}\frac{1}{r}\frac{\mathrm{d}U}{\mathrm{d}r}\boldsymbol{s}\cdot\boldsymbol{l} = \xi(r)\boldsymbol{s}\cdot\boldsymbol{l}.$$

The Hamiltonian:

$$H_{\text{s-o}} = \sum_i \beta_i \boldsymbol{s}_i \cdot \boldsymbol{l}_i = \beta_{LS}\boldsymbol{S}\cdot\boldsymbol{L}.$$

$$H = H_{\text{CF}} + H_{\text{re}} + H_{\text{s-o}}.$$

the total electronic angular momentum: $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$.

$$\therefore \quad \boldsymbol{L}\cdot\boldsymbol{S} = \frac{(\boldsymbol{J}\cdot\boldsymbol{J} - \boldsymbol{L}\cdot\boldsymbol{L} - \boldsymbol{S}\cdot\boldsymbol{S})}{2},$$

$$\therefore \quad [\boldsymbol{J}^2, H] = 0 \quad \text{and} \quad [J_z, H] = 0.$$

Fine structure in the LS-coupling scheme

Spin orbit coupling of electrons

Approximate calculations of relativistic quantum mechanics at low speeds:

$$U_{sl} = \frac{1}{2\mu^2 c^2} \frac{1}{r} \frac{\mathrm{d}U}{\mathrm{d}r} \boldsymbol{s} \cdot \boldsymbol{l} = \xi(r) \boldsymbol{s} \cdot \boldsymbol{l}.$$

The Hamiltonian:

$$H_{\mathrm{s-o}} = \sum_i \beta_i \boldsymbol{s_i} \cdot \boldsymbol{l_i} = \beta_{LS} \boldsymbol{S} \cdot \boldsymbol{L}.$$

$$H = H_{\mathrm{CF}} + H_{\mathrm{re}} + H_{\mathrm{s-o}}.$$

the total electronic angular momentum: $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$.

$$\therefore \quad \boldsymbol{L} \cdot \boldsymbol{S} = \frac{(\boldsymbol{J} \cdot \boldsymbol{J} - \boldsymbol{L} \cdot \boldsymbol{L} - \boldsymbol{S} \cdot \boldsymbol{S})}{2},$$

$$\therefore \quad [\boldsymbol{J}^2, H] = 0 \quad \text{and} \quad [J_z, H] = 0.$$

Fine structure in the LS-coupling scheme

Spin orbit coupling of electrons

Approximate calculations of relativistic quantum mechanics at low speeds:

$$U_{sl} = \frac{1}{2\mu^2 c^2} \frac{1}{r} \frac{dU}{dr} \boldsymbol{s} \cdot \boldsymbol{l} = \xi(r) \boldsymbol{s} \cdot \boldsymbol{l}.$$

The Hamiltonian:

$$H_{\text{s}-\text{o}} = \sum_i \beta_i \boldsymbol{s}_i \cdot \boldsymbol{l}_i = \beta_{LS} \boldsymbol{S} \cdot \boldsymbol{L}.$$

$$H = H_{\text{CF}} + H_{\text{re}} + H_{\text{s}-\text{o}}.$$

the total electronic angular momentum: $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$.

$$\because \quad \boldsymbol{L} \cdot \boldsymbol{S} = \frac{(\boldsymbol{J} \cdot \boldsymbol{J} - \boldsymbol{L} \cdot \boldsymbol{L} - \boldsymbol{S} \cdot \boldsymbol{S})}{2},$$

$$\therefore \quad \left[\boldsymbol{J}^2, H \right] = 0 \quad \text{and} \quad \left[J_z, H \right] = 0.$$

Fine structure in the LS-coupling scheme

Therefore, L_z, S_z are no longer conserved.

$$\text{good quantum numbers} : L, S, J, M_J,$$
$$\text{eigenstates of } H : |LSJM_J\rangle .$$

The energy shift: (degeneracy with respect to M_J)

$$E_{\text{s-o}} = \beta_{LS} \langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle$$
$$= \frac{\beta_{LS}}{2} \{ J(J+1) - L(L+1) - S(S+1) \} .$$

Lande interval rule

The energy interval between adjacent J levels:

$$\Delta E_{\text{FS}} = E_J - E_{J-1} = \beta_{LS} J \propto J.$$

北京大学
PEKING UNIVERSITY

Therefore, L_z, S_z are no longer conserved.

$$\text{good quantum numbers}: L, S, J, M_J,$$
$$\text{eigenstates of } H: |LSJM_J\rangle.$$

The energy shift: (degeneracy with respect to M_J)

$$E_{\text{s}-\text{o}} = \beta_{LS} \langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle$$
$$= \frac{\beta_{LS}}{2} \left\{ J(J+1) - L(L+1) - S(S+1) \right\}.$$

Lande interval rule

The energy interval between adjacent J levels:

$$\Delta E_{\text{FS}} = E_J - E_{J-1} = \beta_{LS} J \propto J.$$

Fine structure in the LS-coupling scheme

Therefore, L_z, S_z are no longer conserved.

$$\text{good quantum numbers}: L, S, J, M_J,$$
$$\text{eigenstates of } H: |LSJM_J\rangle.$$

The energy shift: (degeneracy with respect to M_J)

$$E_{\text{s}-\text{o}} = \beta_{LS} \langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle$$
$$= \frac{\beta_{LS}}{2} \left\{ J(J+1) - L(L+1) - S(S+1) \right\}.$$

Lande interval rule

The energy interval between adjacent J levels:

$$\Delta E_{\text{FS}} = E_J - E_{J-1} = \beta_{LS} J \propto J.$$

$npn'\mathrm{p}\ (n \neq n')$

$$
\begin{array}{c|ccc}
L=0 & 1 & 2 \\
\hline
S=0 & {}^1\mathrm{S}_0 & {}^1\mathrm{P}_1 & {}^1\mathrm{D}_2 \\
1 & {}^3\mathrm{S}_1 & {}^3\mathrm{P}_{210} & {}^3\mathrm{D}_{321}
\end{array}
$$

$npn'\mathrm{p}$		M_S		
		1	0	-1
	2	$(1\uparrow 1\uparrow)$	$(1\uparrow 1\downarrow)(1\downarrow 1\uparrow)$	$(1\downarrow 1\downarrow)$
	1	$(1\uparrow 0\uparrow)(0\uparrow 1\uparrow)$	$(1\uparrow 0\downarrow)(0\uparrow 1\downarrow)(1\downarrow 0\uparrow)(0\downarrow 1\uparrow)$	$(1\downarrow 0\downarrow)(0\downarrow 1\downarrow)$
M_L	0	$(1\uparrow \bar{1}\uparrow)(0\uparrow 0\uparrow)$ $(1\uparrow 1\uparrow)$	$(1\uparrow \bar{1}\downarrow)(0\uparrow 0\downarrow)(\bar{1}\uparrow 1\downarrow)$ $(1\downarrow \bar{1}\uparrow)(0\downarrow 0\uparrow)(\bar{1}\downarrow 1\uparrow)$	$(1\downarrow \bar{1}\downarrow)(0\downarrow 0\downarrow)$ $(1\downarrow 1\downarrow)$
	-1	$(\bar{1}\uparrow 0\uparrow)(0\uparrow \bar{1}\uparrow)$	$(\bar{1}\uparrow 0\downarrow)(0\uparrow \bar{1}\downarrow)(\bar{1}\downarrow 0\uparrow)(0\downarrow \bar{1}\uparrow)$	$(\bar{1}\downarrow 0\downarrow)(0\downarrow \bar{1}\downarrow)$
	-2	$(\bar{1}\uparrow \bar{1}\uparrow)$	$(\bar{1}\uparrow \bar{1}\downarrow)(\bar{1}\downarrow \bar{1}\uparrow)$	$(\bar{1}\downarrow \bar{1}\downarrow)$	a

[a] $\bar{1} = -1$.

$(n\mathrm{p})^2$

For equivalent electrons the Pauli exclusion principle restricts the states.

$(n\mathrm{p})^2$		M_S		
		1	0	−1
M_L	2		$(1\uparrow 1\downarrow)$	
	1	$(1\uparrow 0\uparrow)$	$(1\uparrow 0\downarrow)(1\downarrow 0\uparrow)$	$(1\downarrow 0\downarrow)$
	0	$(1\uparrow \bar{1}\uparrow)$	$(1\uparrow \bar{1}\downarrow)(1\downarrow \bar{1}\uparrow)(0\uparrow 0\downarrow)$	$(1\downarrow \bar{1}\downarrow)$
	−1	$(0\uparrow \bar{1}\uparrow)$	$(0\uparrow \bar{1}\downarrow)(0\downarrow \bar{1}\uparrow)$	$(0\downarrow \bar{1}\downarrow)$
	−2		$(\bar{1}\uparrow \bar{1}\downarrow)$	

Even rule:

$$2|(L+S).$$

$(n\mathrm{p})^2$

For equivalent electrons the Pauli exclusion principle restricts the states.

$(n\mathrm{p})^2$		M_S		
		1	0	-1
M_L	2		$(1\uparrow 1\downarrow)$	
	1	$(1\uparrow 0\uparrow)$	$(1\uparrow 0\downarrow)(1\downarrow 0\uparrow)$	$(1\downarrow 0\downarrow)$
	0	$(1\uparrow \bar{1}\uparrow)$	$(1\uparrow \bar{1}\downarrow)(1\downarrow \bar{1}\uparrow)(0\uparrow 0\downarrow)$	$(1\downarrow \bar{1}\downarrow)$
	-1	$(0\uparrow \bar{1}\uparrow)$	$(0\uparrow \bar{1}\downarrow)(0\downarrow \bar{1}\uparrow)$	$(0\downarrow \bar{1}\downarrow)$
	-2		$(\bar{1}\uparrow \bar{1}\downarrow)$	

Even rule:
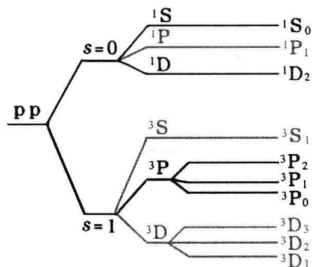
$$2|(L+S).$$

Figure: pp electronic configuration energy levels

Black line: $(n\mathrm{p})^2$,
Gray line: prohibited by Pauli's principle,
All line: $n\mathrm{p}n'\mathrm{p}$.

Hund's rules

1. $S \nearrow E \searrow$;
2. $L \nearrow E \searrow$;
3.
   - Normal order ($J \searrow E \searrow$) : under half shell layer;
   - Anomalous order ($J \nearrow E \searrow$) : over half shell layer.

However, Hund's rules are empirical and there are exceptions. They are more effective in inferring the ground state, with only a few exceptions. Using it to discuss excited states is not very reliable.

Application: determine the ground state

$$m_l = -1 \quad 0 \quad +1$$

C: $1s^2 2s^2 2p^2$ $\boxed{ \; \uparrow \; \uparrow}$ $\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_0$

N: $1s^2 2s^2 2p^3$ $\boxed{\uparrow \; \uparrow \; \uparrow}$ $\Rightarrow S = 3/2, L = 0; J = 3/2 \Rightarrow {}^4S_{3/2}$

O: $1s^2 2s^2 2p^4$ $\boxed{\uparrow \; \uparrow \; \uparrow\downarrow}$ $\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_2$

Hund's rules

1. $S \nearrow$ $E \searrow$;
2. $L \nearrow$ $E \searrow$;
3. ■ Normal order ($J \searrow E \searrow$) : under half shell layer;
   ■ Anomalous order ($J \nearrow E \searrow$) : over half shell layer.

However, Hund's rules are empirical and there are exceptions. They are more effective in inferring the ground state, with only a few exceptions. Using it to discuss excited states is not very reliable.
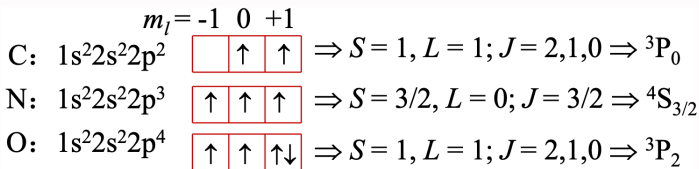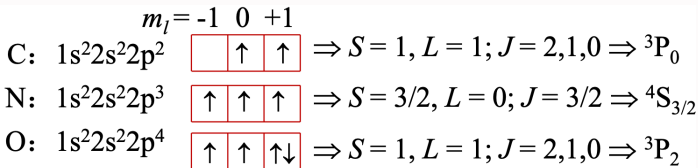
Application: determine the ground state

$$m_l = -1 \quad 0 \quad +1$$

C: $1s^2 2s^2 2p^2$ $\boxed{ \; \uparrow \; \uparrow}$ $\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_0$

N: $1s^2 2s^2 2p^3$ $\boxed{\uparrow \; \uparrow \; \uparrow}$ $\Rightarrow S = 3/2, L = 0; J = 3/2 \Rightarrow {}^4S_{3/2}$

O: $1s^2 2s^2 2p^4$ $\boxed{\uparrow \; \uparrow \; \uparrow\downarrow}$ $\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_2$

Hund's rules

1. $S \nearrow \ E \searrow$;

2. $L \nearrow \ E \searrow$;

3. ■ Normal order ($J \searrow \ E \searrow$) : under half shell layer;

   ■ Anomalous order ($J \nearrow \ E \searrow$) : over half shell layer.

However, Hund's rules are empirical and there are exceptions. They are more effective in inferring the ground state, with only a few exceptions. Using it to discuss excited states is not very reliable.
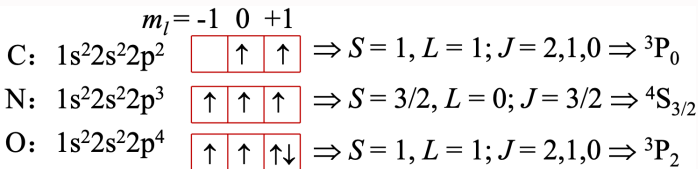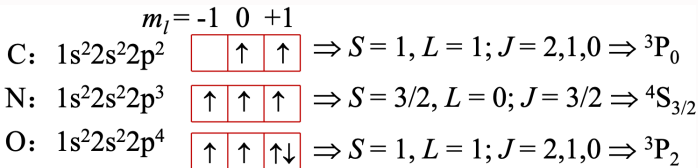
Application: determine the ground state

$$m_l = \text{-1} \quad 0 \quad \text{+1}$$

C : $1s^2 2s^2 2p^2$ | | $\uparrow$ | $\uparrow$ | $\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_0$

N : $1s^2 2s^2 2p^3$ | $\uparrow$ | $\uparrow$ | $\uparrow$ | $\Rightarrow S = 3/2, L = 0; J = 3/2 \Rightarrow {}^4S_{3/2}$

O : $1s^2 2s^2 2p^4$ | $\uparrow$ | $\uparrow$ | $\uparrow\downarrow$ | $\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_2$

Hund's rules

1. $S \nearrow \quad E \searrow$;
2. $L \nearrow \quad E \searrow$;
3.
   - Normal order ($J \searrow \quad E \searrow$) : under half shell layer;
   - Anomalous order ($J \nearrow \quad E \searrow$) : over half shell layer.

However, Hund's rules are empirical and there are exceptions. They are more effective in inferring the ground state, with only a few exceptions. Using it to discuss excited states is not very reliable.
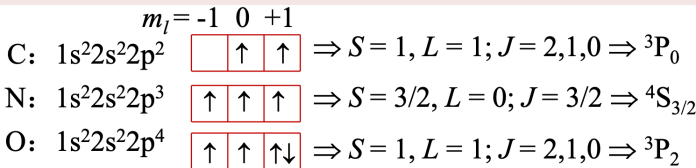
Application: determine the ground state

$$m_l = \text{-1} \quad 0 \quad \text{+1}$$

C: $1s^2 2s^2 2p^2$ [| $\uparrow$ | $\uparrow$] $\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_0$

N: $1s^2 2s^2 2p^3$ [$\uparrow$ | $\uparrow$ | $\uparrow$] $\Rightarrow S = 3/2, L = 0; J = 3/2 \Rightarrow {}^4S_{3/2}$

O: $1s^2 2s^2 2p^4$ [$\uparrow$ | $\uparrow$ | $\uparrow\downarrow$] $\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_2$

Hund's rules

1. $S \nearrow \quad E \searrow$;
2. $L \nearrow \quad E \searrow$;
3.
   - Normal order ($J \searrow \quad E \searrow$) : under half shell layer;
   - Anomalous order ($J \nearrow \quad E \searrow$) : over half shell layer.

However, Hund's rules are empirical and there are exceptions. They are more effective in inferring the ground state, with only a few exceptions. Using it to discuss excited states is not very reliable.

Application: determine the ground state

$$
\begin{array}{rl}
m_l = \text{-1} \quad 0 \quad \text{+1} & \\
\text{C}: 1s^2 2s^2 2p^2 \quad \boxed{ \uparrow \uparrow} & \Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3\text{P}_0 \\
\text{N}: 1s^2 2s^2 2p^3 \quad \boxed{\uparrow \uparrow \uparrow} & \Rightarrow S = 3/2, L = 0; J = 3/2 \Rightarrow {}^4\text{S}_{3/2} \\
\text{O}: 1s^2 2s^2 2p^4 \quad \boxed{\uparrow \uparrow \uparrow\downarrow} & \Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3\text{P}_2
\end{array}
$$

Hund's rules

1. $S \nearrow \quad E \searrow$;
2. $L \nearrow \quad E \searrow$;
3.
   - Normal order ($J \searrow \quad E \searrow$) : under half shell layer;
   - Anomalous order ($J \nearrow \quad E \searrow$) : over half shell layer.

However, Hund's rules are empirical and there are exceptions. They are more effective in inferring the ground state, with only a few exceptions. Using it to discuss excited states is not very reliable.

Application: determine the ground state

$m_l = $ -1 0 +1

C: $1s^2 2s^2 2p^2$ $\quad \boxed{ | \uparrow | \uparrow} \Rightarrow S=1, L=1; J=2,1,0 \Rightarrow {}^3P_0$

N: $1s^2 2s^2 2p^3$ $\quad \boxed{\uparrow | \uparrow | \uparrow} \Rightarrow S=3/2, L=0; J=3/2 \Rightarrow {}^4S_{3/2}$

O: $1s^2 2s^2 2p^4$ $\quad \boxed{\uparrow | \uparrow | \uparrow\downarrow} \Rightarrow S=1, L=1; J=2,1,0 \Rightarrow {}^3P_2$

Theoretical explanation

Generalize the potential expression of spin-orbit coupling to the coupling of any two angular momentum:

$$U_{l_1 l_2} = \frac{1}{2\mu^2 c^2} \frac{1}{r} \frac{\mathrm{d}U}{\mathrm{d}r} \boldsymbol{l}_1 \cdot \boldsymbol{l}_2, \quad (\boldsymbol{L} = \boldsymbol{l}_1 + \boldsymbol{l}_2)$$

The contribution of the coupling of angular momentum to the interaction potential:

$$\langle \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \rangle = \frac{1}{2} \big[L(L+1) - l_1(l_1+1) - l_2(l_2+1) \big] \hbar^2.$$

Apparently, $L \nearrow \ \langle \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \rangle \nearrow$, so the key is $\frac{\mathrm{d}U}{\mathrm{d}r} ? 0$.

Theoretical explanation

Generalize the potential expression of spin-orbit coupling to the coupling of any two angular momentum:

$$U_{l_1 l_2} = \frac{1}{2\mu^2 c^2} \frac{1}{r} \frac{\mathrm{d}U}{\mathrm{d}r} \boldsymbol{l}_1 \cdot \boldsymbol{l}_2, \quad (\boldsymbol{L} = \boldsymbol{l}_1 + \boldsymbol{l}_2)$$

The contribution of the coupling of angular momentum to the interaction potential:

$$\langle \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \rangle = \frac{1}{2} \big[L(L+1) - l_1(l_1+1) - l_2(l_2+1) \big] \hbar^2.$$

Apparently, $L \nearrow \ \langle \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \rangle \nearrow$, so the key is $\dfrac{\mathrm{d}U}{\mathrm{d}r}$? 0.

Theoretical explanation

Generalize the potential expression of spin-orbit coupling to the coupling of any two angular momentum:

$$U_{l_1 l_2} = \frac{1}{2\mu^2 c^2} \frac{1}{r} \frac{dU}{dr} \boldsymbol{l}_1 \cdot \boldsymbol{l}_2, \quad (\boldsymbol{L} = \boldsymbol{l}_1 + \boldsymbol{l}_2)$$

The contribution of the coupling of angular momentum to the interaction potential:

$$\langle \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \rangle = \frac{1}{2} \big[L(L+1) - l_1(l_1+1) - l_2(l_2+1) \big] \hbar^2.$$

Apparently, $L \nearrow \langle \boldsymbol{l}_1 \cdot \boldsymbol{l}_2 \rangle \nearrow$, so the key is $\dfrac{dU}{dr}$? 0.

Hund's rules

Theoretical explanation

- Electron-electron Coulomb repulsion: 1&2

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{e^2}{r}\right) \propto -\frac{1}{r^2} < 0,$$

- Electron-nucleon Coulomb attraction: 3-normal order

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(-\frac{e^2}{r}\right) \propto \frac{1}{r^2} > 0,$$

- Hole-nucleon Coulomb repulsion: 3-anomalous order

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{e^2}{r}\right) \propto -\frac{1}{r^2} < 0.$$

Hund's rules

Theoretical explanation

- Electron-electron Coulomb repulsion: 1&2

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{e^2}{r}\right) \propto -\frac{1}{r^2} < 0,$$

- Electron-nucleon Coulomb attraction: 3-normal order

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(-\frac{e^2}{r}\right) \propto \frac{1}{r^2} > 0,$$

- Hole-nucleon Coulomb repulsion: 3-anomalous order

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{e^2}{r}\right) \propto -\frac{1}{r^2} < 0.$$

Hund's rules

Theoretical explanation

- Electron-electron Coulomb repulsion: 1&2

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{e^2}{r}\right) \propto -\frac{1}{r^2} < 0,$$

- Electron-nucleon Coulomb attraction: 3-normal order

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(-\frac{e^2}{r}\right) \propto \frac{1}{r^2} > 0,$$

- Hole-nucleon Coulomb repulsion: 3-anomalous order

$$\frac{\mathrm{d}U}{\mathrm{d}r} \propto \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{e^2}{r}\right) \propto -\frac{1}{r^2} < 0.$$

Content

Hamiltonian

$H_{\mathrm{s-o}} \gg H_{\mathrm{re}}$:

$$H = H_{\mathrm{CF}} + H_{\mathrm{s-o}}$$

$$= \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + V_{\mathrm{CF}}(r_i) \right\} + \sum_{i=1}^{N} \xi_i(r_i) \boldsymbol{l}_1 \cdot \boldsymbol{s}_i$$

$$= \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + V_{\mathrm{CF}}(r_i) + \xi_i(r_i) \boldsymbol{l}_1 \cdot \boldsymbol{s}_i \right\}.$$

Approximate to an independent particle system.

Use a complete set of quantum numbers for each electron to characterize quantum states: eigenstates of $H_{\mathrm{s-o}}$: $\prod_{i}^{N} |n_i l_i j_i (m_j)_i\rangle$.

The jj-coupling scheme

Hamiltonian

$H_{\mathrm{s-o}} \gg H_{\mathrm{re}}$:

$$H = H_{\mathrm{CF}} + H_{\mathrm{s-o}}$$

$$= \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + V_{\mathrm{CF}}\left(r_i\right) \right\} + \sum_{i=1}^{N} \xi_i(r_i)\boldsymbol{l}_1 \cdot \boldsymbol{s}_i$$

$$= \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m}\nabla_i^2 + V_{\mathrm{CF}}\left(r_i\right) + \xi_i(r_i)\boldsymbol{l}_1 \cdot \boldsymbol{s}_i \right\}.$$

Approximate to an independent particle system.

Use a complete set of quantum numbers for each electron to characterize quantum states: eigenstates of $H_{\mathrm{s-o}}$: $\prod_{i}^{N} |n_i l_i j_i (m_j)_i\rangle$.

The jj-coupling scheme

Hamiltonian

$H_{s-o} \gg H_{re}$:

$$H = H_{CF} + H_{s-o}$$

$$= \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{CF}(r_i) \right\} + \sum_{i=1}^{N} \xi_i(r_i) \boldsymbol{l}_1 \cdot \boldsymbol{s}_i$$

$$= \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{CF}(r_i) + \xi_i(r_i) \boldsymbol{l}_1 \cdot \boldsymbol{s}_i \right\}.$$

Approximate to an independent particle system.

Use a complete set of quantum numbers for each electron to characterize quantum states: eigenstates of H_{s-o}: $\prod_{i}^{N} |n_i l_i j_i (m_j)_i\rangle$.

The jj-coupling scheme

Energy:

$$E_{\text{s-o}} = \sum_i^N \langle n_i l_i j_i (m_j)_i | H_{\text{s-o}} | n_i l_i j_i (m_j)_i \rangle$$

$$= \frac{1}{2} \sum_i^N \xi_{i n_i l_i}(r_i)[j_i(j_i+1) - l_i(l_i+1) - \frac{3}{4}].$$

$$(\xi_{i n_i l_i}(r_i) = \langle n_i l_i | \xi_i(r_i) | n_i l_i \rangle \,.)$$

Therefore,

good quantum numbers : $j_1, j_2, \cdots, j_i, \cdots, j_N, J$.

Label:

$$(j_1, j_2, \cdots, j_i, \cdots, j_N)_J.$$

Considering H_{re}, the energy levels will split according to the total angular momentum $\boldsymbol{J}$. (degeneracy with respect to M_J)

The jj-coupling scheme

Energy:

$$E_{\text{s-o}} = \sum_i^N \langle n_i l_i j_i (m_j)_i | H_{\text{s-o}} | n_i l_i j_i (m_j)_i \rangle$$

$$= \frac{1}{2} \sum_i^N \xi_{i n_i l_i}(r_i)[j_i(j_i+1) - l_i(l_i+1) - \frac{3}{4}].$$

$$(\xi_{i n_i l_i}(r_i) = \langle n_i l_i | \xi_i(r_i) | n_i l_i \rangle .)$$

Therefore,

good quantum numbers : $j_1, j_2, \cdots, j_i, \cdots, j_N, J$.

Label:

$$(j_1, j_2, \cdots, j_i, \cdots, j_N)_J.$$

Considering H_{re}, the energy levels will split according to the total angular momentum $\boldsymbol{J}$. (degeneracy with respect to M_J)

The jj-coupling scheme

Energy:

$$E_{\text{s-o}} = \sum_i^N \langle n_i l_i j_i (m_j)_i | H_{\text{s-o}} | n_i l_i j_i (m_j)_i \rangle$$

$$= \frac{1}{2} \sum_i^N \xi_{i n_i l_i}(r_i) [j_i(j_i+1) - l_i(l_i+1) - \frac{3}{4}].$$

$$(\xi_{i n_i l_i}(r_i) = \langle n_i l_i | \xi_i(r_i) | n_i l_i \rangle \,.)$$

Therefore,

good quantum numbers : $j_1, j_2, \cdots, j_i, \cdots, j_N, J$.

Label:

$$(j_1, j_2, \cdots, j_i, \cdots, j_N)_J.$$

Considering H_{re}, the energy levels will split according to the total angular momentum $\boldsymbol{J}$. (degeneracy with respect to M_J)

The jj-coupling scheme

Energy:

$$E_{\text{s-o}} = \sum_i^N \langle n_i l_i j_i (m_j)_i | H_{\text{s-o}} | n_i l_i j_i (m_j)_i \rangle$$

$$= \frac{1}{2} \sum_i^N \xi_{i n_i l_i}(r_i) [j_i(j_i+1) - l_i(l_i+1) - \frac{3}{4}].$$

$$(\xi_{i n_i l_i}(r_i) = \langle n_i l_i | \xi_i(r_i) | n_i l_i \rangle.)$$

Therefore,

good quantum numbers : $j_1, j_2, \cdots, j_i, \cdots, j_N, J$.

Label:

$$(j_1, j_2, \cdots, j_i, \cdots, j_N)_J.$$

Considering H_{re}, the energy levels will split according to the total angular momentum $\boldsymbol{J}$. (degeneracy with respect to M_J)

$npn'p$ ($n \neq n'$)

$npn'p$		j_1, j_2			
		$\frac{3}{2},\frac{3}{2}$	$\frac{3}{2},\frac{1}{2}$	$\frac{1}{2},\frac{3}{2}$	$\frac{1}{2},\frac{1}{2}$
M_J	3	$(\frac{3}{2},\frac{3}{2})$			
	2	$(\frac{3}{2},\frac{1}{2})(\frac{1}{2},\frac{3}{2})$	$(\frac{3}{2},\frac{1}{2})$	$(\frac{1}{2},\frac{3}{2})$	
	1	$(\frac{3}{2},-\frac{1}{2})(-\frac{1}{2},\frac{3}{2})(\frac{1}{2},\frac{1}{2})$	$(\frac{3}{2},-\frac{1}{2})(\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2},\frac{1}{2})(-\frac{1}{2},\frac{3}{2})$	$(\frac{1}{2},\frac{1}{2})$
	0	$(\frac{3}{2},-\frac{3}{2})(-\frac{3}{2},\frac{3}{2})(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{1}{2})$	$(\frac{3}{2},-\frac{3}{2})(-\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{3}{2})$	$(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{1}{2})$
	−1	$(\frac{1}{2},-\frac{3}{2})(-\frac{3}{2},\frac{1}{2})(-\frac{1}{2},-\frac{1}{2})$	$(-\frac{1}{2},-\frac{1}{2})(-\frac{3}{2},\frac{1}{2})$	$(-\frac{1}{2},-\frac{1}{2})(\frac{1}{2},-\frac{3}{2})$	$(-\frac{1}{2},-\frac{1}{2})$
	−2	$(-\frac{3}{2},-\frac{1}{2})(-\frac{1}{2},-\frac{3}{2})$	$(-\frac{3}{2},-\frac{1}{2})$	$(-\frac{1}{2},-\frac{3}{2})$	
	−3	$(-\frac{3}{2},-\frac{3}{2})$			
J		3, 2, 1, 0	2, 1	2, 1	1, 0

$(np)^2$

For equivalent electrons the Pauli exclusion principle restricts the states.

$(np)^2$		j_1, j_2		
		$\frac{3}{2},\frac{3}{2}$	$\frac{3}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2}$
M_J	2	$(\frac{3}{2},\frac{1}{2})$	$(\frac{3}{2},\frac{1}{2})$	
	1	$(\frac{3}{2},-\frac{1}{2})$	$(\frac{3}{2},-\frac{1}{2})(\frac{1}{2},\frac{1}{2})$	
	0	$(\frac{3}{2},-\frac{3}{2})(\frac{1}{2},-\frac{1}{2})$	$(\frac{3}{2},-\frac{1}{2})(-\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2},-\frac{1}{2})$
	−1	$(-\frac{3}{2},\frac{1}{2})$	$(-\frac{3}{2},\frac{1}{2})(-\frac{1}{2},-\frac{1}{2})$	
	−2	$(-\frac{3}{2},-\frac{1}{2})$	$(-\frac{3}{2},-\frac{1}{2})$	
J		2, 0	2, 1	0

Example: pp electronic configuration

$np n'p$ $(n \neq n')$

$npn'p$	M_J	$\frac{3}{2},\frac{3}{2}$	$\frac{3}{2},\frac{1}{2}$	$\frac{1}{2},\frac{3}{2}$	$\frac{1}{2},\frac{1}{2}$
	3	$(\frac{3}{2},\frac{3}{2})$			
	2	$(\frac{3}{2},\frac{1}{2})(\frac{1}{2},\frac{3}{2})$	$(\frac{3}{2},\frac{1}{2})$	$(\frac{1}{2},\frac{3}{2})$	
	1	$(\frac{3}{2},-\frac{1}{2})(-\frac{1}{2},\frac{3}{2})(\frac{1}{2},\frac{1}{2})$	$(\frac{3}{2},-\frac{1}{2})(\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{3}{2})$	$(\frac{1}{2},\frac{1}{2})$
M_J	0	$(\frac{3}{2},-\frac{3}{2})(-\frac{3}{2},\frac{3}{2})(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{1}{2})$
	−1	$(\frac{1}{2},-\frac{3}{2})(-\frac{3}{2},\frac{1}{2})(-\frac{1}{2},-\frac{1}{2})$	$(-\frac{1}{2},-\frac{1}{2})(-\frac{3}{2},\frac{1}{2})$	$(-\frac{3}{2},\frac{1}{2})(\frac{1}{2},-\frac{3}{2})$	$(-\frac{1}{2},-\frac{1}{2})$
	−2	$(-\frac{3}{2},-\frac{1}{2})(-\frac{1}{2},-\frac{3}{2})$	$(-\frac{3}{2},-\frac{1}{2})$	$(-\frac{1}{2},-\frac{3}{2})$	
	−3	$(-\frac{3}{2},-\frac{3}{2})$			
J		3, 2, 1, 0	2, 1	2, 1	1, 0

$(np)^2$

For equivalent electrons the Pauli exclusion principle restricts the states.

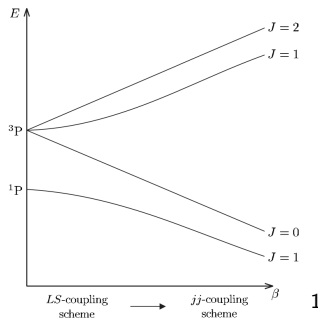| $(np)^2$	M_J	$\frac{3}{2},\frac{3}{2}$	$\frac{3}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2}$
	2	$(\frac{3}{2},\frac{1}{2})$	$(\frac{3}{2},\frac{1}{2})$	
	1	$(\frac{3}{2},-\frac{1}{2})$	$(\frac{3}{2},-\frac{1}{2})(\frac{1}{2},\frac{1}{2})$	
M_J	0	$(\frac{3}{2},-\frac{3}{2})(\frac{1}{2},-\frac{1}{2})$	$(\frac{1}{2},-\frac{1}{2})(-\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2},-\frac{1}{2})$
	−1	$(-\frac{3}{2},\frac{1}{2})$	$(-\frac{3}{2},\frac{1}{2})(-\frac{1}{2},-\frac{1}{2})$	
	−2	$(-\frac{3}{2},-\frac{1}{2})$	$(-\frac{3}{2},-\frac{1}{2})$	
J		2, 0	2, 1	0

Content

Figure: sp configuration

As β increases further the spin–orbit and residual electrostatic interactions become comparable and the LS-coupling scheme ceases to be a good approximation: the interval rule and (LS-coupling) selection rules break down. At large β the jj-coupling scheme is appropriate.

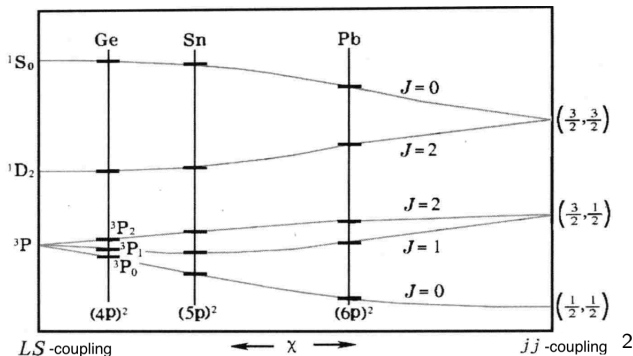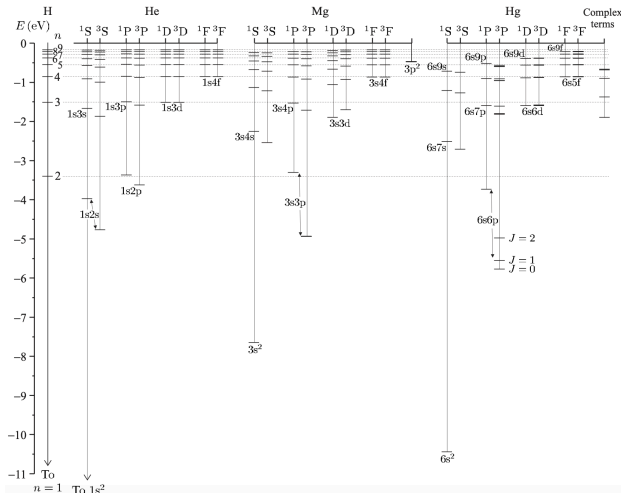[1] β: the spin–orbit interaction parameter.
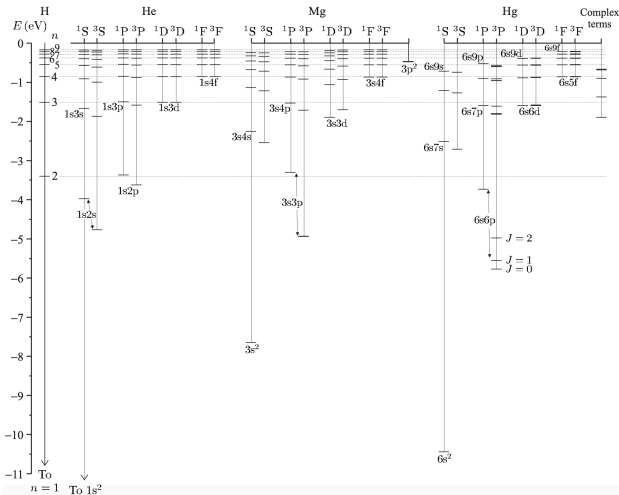
Figure: p^2 configuration

A evident transition by χ.

---

[2]χ: characteristic parameter.

Even for Hg, the LS-coupling scheme gives a closer approximation than the jj-coupling scheme.

3s3p, Mg	6s6p, Hg
2.1850	3.76
2.1870	3.94
2.1911	4.40
3.5051	5.40

Table: E/m^{-1}

e.g. for the 6s6p configuration the $E_{\mathrm{re}} > E_{\mathrm{s-o}}$ but the interval rule is not obeyed because the spin-orbit interaction is not very small compared to the residual electrostatic interaction.

Even for Hg, the LS-coupling scheme gives a closer approximation than the jj-coupling scheme.

In experiment
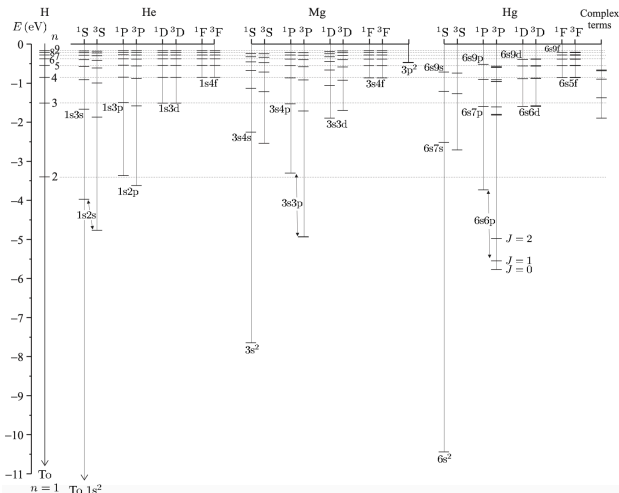
J	E (m^{-1})
2	16908687
1	16908694
0	16908793
1	17113500

Table: The 1s2p configuration in helium

The interval rule is not obeyed: This occurs in helium because spin–spin and spin–other-orbit interactions have an energy comparable with that of the spin–orbit interaction.

Even for Hg, the LS-coupling scheme gives a closer approximation than the jj-coupling scheme.

Content

Electric dipole selection rules

Single electron

From conservation laws and quantum mechanics calculations:

$$\begin{cases} \Delta j = 0, \pm 1 & (j = 0 \nleftrightarrow j' = 0), \\ \Delta m_j = 0, \pm 1, & (m_j = 0 \nleftrightarrow m_{j'} = 0 \text{ if } \Delta j = 0), \\ \Delta l = \pm 1, \\ \Delta m_l = 0, \pm 1. \end{cases}$$

LS-coupling scheme:

$$
\begin{cases}
\Delta J = 0, \pm 1 & (J = 0 \nleftrightarrow J' = 0), \\
\Delta M_J = 0, \pm 1 & (M_J = 0 \nrightarrow M_{J'} = 0 \text{ if } \Delta J = 0), \\
\text{Parity changes}, \\
\Delta l = \pm 1 & \text{One electron jump}, \\
\Delta L = 0^1, \pm 1 & (L = 0 \nleftrightarrow L' = 0), \\
\Delta S = 0^2.
\end{cases}
$$

1. $\Delta L = 0$ is possible in principle, but more than one electron must be excited to a high-energy state.

2. Exception: In the mercury atom, however, transitions with $\Delta S = 1$ occur, such as $6s^2\ {}^1S_0 - 6s6p\ {}^3P_1$, that gives a so-called intercombination line with a wavelength of 254 nm.

LS-coupling scheme:

$$\begin{cases} \Delta J = 0, \pm 1 & (J = 0 \not\leftrightarrow J' = 0), \\ \Delta M_J = 0, \pm 1 & (M_J = 0 \not\rightarrow M_{J'} = 0 \text{ if } \Delta J = 0), \\ \text{Parity changes,} \\ \Delta l = \pm 1 & \text{One electron jump,} \\ \Delta L = 0^1, \pm 1 & (L = 0 \not\leftrightarrow L' = 0), \\ \Delta S = 0^2. \end{cases}$$

1.$\Delta L = 0$ is possible in principle, but more than one electron must be excited to a high-energy state.

2.Exception: In the mercury atom, however, transitions with $\Delta S = 1$ occur, such as $6s^2\ ^1S_0 - 6s6p\ ^3P_1$, that gives a so-called intercombination line with a wavelength of 254 nm.

Electric dipole selection rules

LS-coupling scheme:

$$\begin{cases}
\Delta J = 0, \pm 1 & (J = 0 \not\leftrightarrow J' = 0), \\
\Delta M_J = 0, \pm 1 & (M_J = 0 \not\rightarrow M_{J'} = 0 \text{ if } \Delta J = 0), \\
\text{Parity changes}, \\
\Delta l = \pm 1 & \text{One electron jump}, \\
\Delta L = 0^1, \pm 1 & (L = 0 \not\leftrightarrow L' = 0), \\
\Delta S = 0^2.
\end{cases}$$

1. $\Delta L = 0$ is possible in principle, but more than one electron must be excited to a high-energy state.

2. Exception: In the mercury atom, however, transitions with $\Delta S = 1$ occur, such as $6s^2\ ^1S_0 - 6s6p\ ^3P_1$, that gives a so-called intercombination line with a wavelength of 254 nm.

Electric dipole selection rules

Single electron

From conservation laws and quantum mechanics calculations:

$$\begin{cases} \Delta j = 0, \pm 1 & (j = 0 \nleftrightarrow j' = 0), \\ \Delta m_j = 0, \pm 1, & (m_j = 0 \nleftrightarrow m_{j'} = 0 \text{ if } \Delta j = 0), \\ \Delta l = \pm 1, \\ \Delta m_l = 0, \pm 1. \end{cases}$$

jj-coupling scheme (two electrons) :

$$\begin{cases} \Delta j_1 = 0, \quad \Delta j_2 = 0, \pm 1, \quad \text{or} \quad \Delta j_1 = 0, \pm 1, \quad \Delta j_2 = 0, \\ \Delta J = 0, \pm 1 \quad (J = 0 \nleftrightarrow J' = 0), \end{cases}$$

In fact, many elements fall between these two extreme situations, and the selection rules on both sides are not strictly followed.

Electric dipole selection rules

Single electron

From conservation laws and quantum mechanics calculations:

$$\begin{cases} \Delta j = 0, \pm 1 & (j = 0 \nleftrightarrow j' = 0), \\ \Delta m_j = 0, \pm 1, & (m_j = 0 \nleftrightarrow m_{j'} = 0 \text{ if } \Delta j = 0), \\ \Delta l = \pm 1, \\ \Delta m_l = 0, \pm 1. \end{cases}$$

jj-coupling scheme (two electrons) :

$$\begin{cases} \Delta j_1 = 0, & \Delta j_2 = 0, \pm 1, \quad \text{or} \qquad \Delta j_1 = 0, \pm 1, \quad \Delta j_2 = 0, \\ \Delta J = 0, \pm 1 & (J = 0 \nleftrightarrow J' = 0), \end{cases}$$

In fact, many elements fall between these two extreme situations, and the selection rules on both sides are not strictly followed.

Magnetic dipole selection rules

According to the multipole expansion of electromagnetic interactions, the magnetic dipole interaction can be described as the interaction between magnetic moment and vector radius, with the coefficient being the first-order spherical harmonic function.

Therefore, the interaction can be expressed as

$$H' \propto \cos\theta \, Y_{10}(\theta, \phi) \propto Y_{00}(\theta, \phi).$$

Therefore, apart from having the same selection rules as electric dipole transitions, there are also angular momentum selection rules:

$$\Delta l = 0.$$

Directly generalized to multi-electron atoms:

$$\Delta n = 0, \begin{cases} \Delta L = 0, & \Delta S = 0, \\ \Delta J = 0, \pm 1, & \Delta M_J = 0, \pm 1. \end{cases}$$

Magnetic dipole selection rules

According to the multipole expansion of electromagnetic interactions, the magnetic dipole interaction can be described as the interaction between magnetic moment and vector radius, with the coefficient being the first-order spherical harmonic function.

Therefore, the interaction can be expressed as

$$H' \propto \cos\theta\, Y_{10}(\theta, \phi) \propto Y_{00}(\theta, \phi).$$

Therefore, apart from having the same selection rules as electric dipole transitions, there are also angular momentum selection rules:

$$\Delta l = 0.$$

Directly generalized to multi-electron atoms:

$$\Delta n = 0, \begin{cases} \Delta L = 0, & \Delta S = 0, \\ \Delta J = 0, \pm 1, & \Delta M_J = 0, \pm 1. \end{cases}$$

Magnetic dipole selection rules

According to the multipole expansion of electromagnetic interactions, the magnetic dipole interaction can be described as the interaction between magnetic moment and vector radius, with the coefficient being the first-order spherical harmonic function.

Therefore, the interaction can be expressed as

$$H' \propto \cos\theta \, Y_{10}(\theta, \phi) \propto Y_{00}(\theta, \phi).$$

Therefore, apart from having the same selection rules as electric dipole transitions, there are also angular momentum selection rules:

$$\Delta l = 0.$$

Directly generalized to multi-electron atoms:

$$\Delta n = 0, \begin{cases} \Delta L = 0, & \Delta S = 0, \\ \Delta J = 0, \pm 1, & \Delta M_J = 0, \pm 1. \end{cases}$$

Content

Original concepts

A atomic spectral lines split in an external magnetic field:

$$\begin{cases} 3 : \text{The normal Zeeman effect.} \\ \text{the other} : \text{The anomalous Zeeman effect.} \end{cases}$$

Modern:

In a strong field: Paschen-Back effect.

In a weak field:

$$\begin{cases} 3 : \text{The normal Zeeman effect.} \\ \text{the other} : \text{The anomalous Zeeman effect.} \end{cases}$$

Original concepts

A atomic spectral lines split in an external magnetic field:

$$\begin{cases} 3 : \text{The normal Zeeman effect.} \\ \text{the other} : \text{The anomalous Zeeman effect.} \end{cases}$$

Modern:

In a strong field: Paschen-Back effect.

In a weak field:

$$\begin{cases} 3 : \text{The normal Zeeman effect.} \\ \text{the other} : \text{The anomalous Zeeman effect.} \end{cases}$$

The Paschen-Back effect

For LS-coupling scheme, the atom's magnetic moment:

$$\boldsymbol{\mu} = -\mu_{\mathrm{B}}\boldsymbol{L} - g_s\mu_{\mathrm{B}}\boldsymbol{S}.$$

The interaction of the atom with an external magnetic field is described by

$$H_{\mathrm{ZE}} = -\boldsymbol{\mu} \cdot \boldsymbol{B}.$$

In a strong field: consider total magnetic moment along the z-direction

$$\mu_z = \mu_{sz} + \mu_{lz} = -2\mu_{\mathrm{B}}m_s - \mu_{\mathrm{B}}m_l = -(2m_s + m_l)\mu_{\mathrm{B}}.$$

Energy:

$$E_{\mathrm{ZE}} = -\mu_z B = (2m_s + m_l)\mu_{\mathrm{B}}.$$

Selection rules

$$\begin{cases} \Delta m_s = 0 \\ \Delta m_l = 0, \pm 1 \end{cases}$$

The Paschen-Back effect

For LS-coupling scheme, the atom's magnetic moment:

$$\boldsymbol{\mu} = -\mu_{\mathrm{B}}\boldsymbol{L} - g_s\mu_{\mathrm{B}}\boldsymbol{S}.$$

The interaction of the atom with an external magnetic field is described by

$$H_{\mathrm{ZE}} = -\boldsymbol{\mu} \cdot \boldsymbol{B}.$$

In a strong field: consider total magnetic moment along the z-direction

$$\mu_z = \mu_{sz} + \mu_{lz} = -2\mu_{\mathrm{B}}m_s - \mu_{\mathrm{B}}m_l = -(2m_s + m_l)\mu_{\mathrm{B}}.$$

Energy:

$$E_{\mathrm{ZE}} = -\mu_z B = (2m_s + m_l)\mu_{\mathrm{B}}.$$

Selection rules

$$\begin{cases} \Delta m_s = 0 \\ \Delta m_l = 0, \pm 1 \end{cases}$$

The Paschen-Back effect

For LS-coupling scheme, the atom's magnetic moment:

$$\boldsymbol{\mu} = -\mu_{\mathrm{B}}\boldsymbol{L} - g_s\mu_{\mathrm{B}}\boldsymbol{S}.$$

The interaction of the atom with an external magnetic field is described by

$$H_{\mathrm{ZE}} = -\boldsymbol{\mu} \cdot \boldsymbol{B}.$$

In a strong field: consider total magnetic moment along the z-direction

$$\mu_z = \mu_{sz} + \mu_{lz} = -2\mu_{\mathrm{B}}m_s - \mu_{\mathrm{B}}m_l = -(2m_s + m_l)\mu_{\mathrm{B}}.$$

Energy:

$$E_{\mathrm{ZE}} = -\mu_{\mathrm{z}}B = (2m_s + m_l)\mu_{\mathrm{B}}.$$

Selection rules

$$\begin{cases} \Delta m_s = 0 \\ \Delta m_l = 0, \pm 1 \end{cases}$$

The Paschen-Back effect

For LS-coupling scheme, the atom's magnetic moment:

$$\boldsymbol{\mu} = -\mu_{\mathrm{B}}\boldsymbol{L} - g_s\mu_{\mathrm{B}}\boldsymbol{S}.$$

The interaction of the atom with an external magnetic field is described by

$$H_{\mathrm{ZE}} = -\boldsymbol{\mu} \cdot \boldsymbol{B}.$$

In a strong field: consider total magnetic moment along the z-direction

$$\mu_z = \mu_{sz} + \mu_{lz} = -2\mu_{\mathrm{B}}m_s - \mu_{\mathrm{B}}m_l = -(2m_s + m_l)\mu_{\mathrm{B}}.$$

Energy:

$$E_{\mathrm{ZE}} = -\mu_{\mathrm{z}}B = (2m_s + m_l)\mu_{\mathrm{B}}.$$

Selection rules

$$\begin{cases} \Delta m_s = 0 \\ \Delta m_l = 0, \pm 1 \end{cases}$$

The Paschen-Back effect

For LS-coupling scheme, the atom's magnetic moment:

$$\boldsymbol{\mu} = -\mu_{\mathrm{B}}\boldsymbol{L} - g_s\mu_{\mathrm{B}}\boldsymbol{S}.$$

The interaction of the atom with an external magnetic field is described by

$$H_{\mathrm{ZE}} = -\boldsymbol{\mu} \cdot \boldsymbol{B}.$$

In a strong field: consider total magnetic moment along the z-direction

$$\mu_z = \mu_{sz} + \mu_{lz} = -2\mu_{\mathrm{B}}m_s - \mu_{\mathrm{B}}m_l = -(2m_s + m_l)\mu_{\mathrm{B}}.$$

Energy:

$$E_{\mathrm{ZE}} = -\mu_z B = (2m_s + m_l)\mu_{\mathrm{B}}.$$

Selection rules

$$\begin{cases} \Delta m_s = 0 \\ \Delta m_l = 0, \pm 1 \end{cases}$$

Figure: $m_l = 1, m_s = -\dfrac{1}{2}, m_j = \dfrac{1}{2}$ & $m_l = -1, m_s = \dfrac{1}{2}, m_j = -\dfrac{1}{2}$ are degenerate

The Zeeman effect

In weak magnetic field, Hamiltonian:

$$H_{\text{ZE}} = -\frac{\langle \boldsymbol{\mu} \cdot \boldsymbol{J} \rangle}{J(J+1)} \boldsymbol{J} \cdot \boldsymbol{B} = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)} \mu_{\text{B}} B J_z.$$

Energy:

$$E_{\text{ZE}} = g_J \mu_{\text{B}} B M_J.$$

Lande g-factor:

$$g_J = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)}.$$

Assuming that $g_s \simeq 2$:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

The Zeeman effect

In weak magnetic field, Hamiltonian:

$$H_{\mathrm{ZE}} = -\frac{\langle \boldsymbol{\mu} \cdot \boldsymbol{J} \rangle}{J(J+1)} \boldsymbol{J} \cdot \boldsymbol{B} = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)} \mu_{\mathrm{B}} B J_z.$$

Energy:

$$E_{\mathrm{ZE}} = g_J \mu_{\mathrm{B}} B M_J.$$

Lande g-factor:

$$g_J = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)}.$$

Assuming that $g_s \simeq 2$:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

The Zeeman effect

In weak magnetic field, Hamiltonian:

$$H_{\mathrm{ZE}} = -\frac{\langle \boldsymbol{\mu} \cdot \boldsymbol{J} \rangle}{J(J+1)} \boldsymbol{J} \cdot \boldsymbol{B} = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)} \mu_{\mathrm{B}} B J_z.$$

Energy:

$$E_{\mathrm{ZE}} = g_J \mu_{\mathrm{B}} B M_J.$$

Lande g-factor:

$$g_J = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)}.$$

Assuming that $g_s \simeq 2$:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

The Zeeman effect

In weak magnetic field, Hamiltonian:

$$H_{\mathrm{ZE}} = -\frac{\langle \boldsymbol{\mu} \cdot \boldsymbol{J} \rangle}{J(J+1)} \boldsymbol{J} \cdot \boldsymbol{B} = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)} \mu_{\mathrm{B}} B J_z.$$

Energy:

$$E_{\mathrm{ZE}} = g_J \mu_{\mathrm{B}} B M_J.$$

Lande g-factor:

$$g_J = \frac{\langle \boldsymbol{L} \cdot \boldsymbol{J} \rangle + g_s \langle \boldsymbol{S} \cdot \boldsymbol{J} \rangle}{J(J+1)}.$$

Assuming that $g_s \simeq 2$:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

The Zeeman effect

No magnetic field

Consider $2 \to 1$:

$$h\nu = E_2 - E_1.$$

External magnetic field $\boldsymbol{B}$:

$$E_2' = E_2 + g_2 M_{J2} \mu_{\mathrm{B}} B, \quad E_1' = E_1 + g_1 M_{J1} \mu_{\mathrm{B}} B.$$

Spectral line splitting:

$$E_2' - E_1' = h\nu + (g_2 M_{J2} - g_1 M_{J1}) \mu_{\mathrm{B}} B.$$

Selection rules

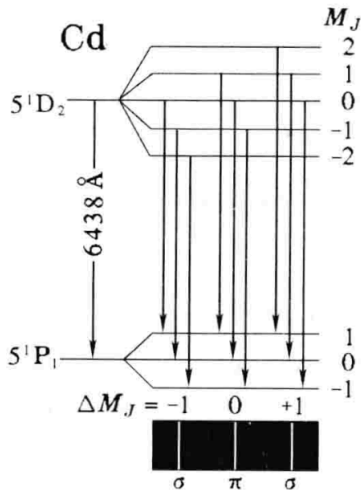$$\Delta M_J = 0, \pm 1.$$

The Zeeman effect

No magnetic field

Consider $2 \to 1$:

$$h\nu = E_2 - E_1.$$

External magnetic field $\boldsymbol{B}$:

$$E'_2 = E_2 + g_2 M_{J2}\mu_{\text{B}}B, \quad E'_1 = E_1 + g_1 M_{J1}\mu_{\text{B}}B.$$

Spectral line splitting:

$$E'_2 - E'_1 = h\nu + (g_2 M_{J2} - g_1 M_{J1})\,\mu_{\text{B}}B.$$

Selection rules

$$\Delta M_J = 0, \pm 1.$$

The Zeeman effect

No magnetic field

Consider $2 \to 1$:

$$h\nu = E_2 - E_1.$$

External magnetic field $\boldsymbol{B}$:

$$E'_2 = E_2 + g_2 M_{J2} \mu_{\mathrm{B}} B, \quad E'_1 = E_1 + g_1 M_{J1} \mu_{\mathrm{B}} B.$$

Spectral line splitting:

$$E'_2 - E'_1 = h\nu + \left(g_2 M_{J2} - g_1 M_{J1} \right) \mu_{\mathrm{B}} B.$$

Selection rules

$$\Delta M_J = 0, \pm 1.$$

The Zeeman effect

No magnetic field

Consider $2 \rightarrow 1$:

$$h\nu = E_2 - E_1.$$

External magnetic field $\boldsymbol{B}$:

$$E_2' = E_2 + g_2 M_{J2} \mu_{\mathrm{B}} B, \quad E_1' = E_1 + g_1 M_{J1} \mu_{\mathrm{B}} B.$$

Spectral line splitting:

$$E_2' - E_1' = h\nu + (g_2 M_{J2} - g_1 M_{J1}) \mu_{\mathrm{B}} B.$$

Selection rules

$$\Delta M_J = 0, \pm 1.$$

Figure: Cd $5^1D_2 \rightarrow 5^1P_1 : S_1 = S_2 = 0 \Rightarrow g_1 = g_2 = 1$
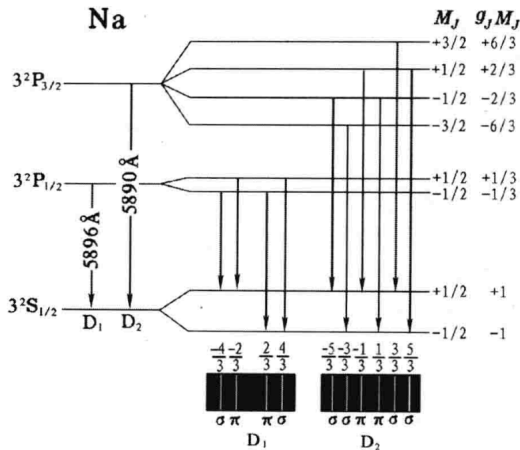
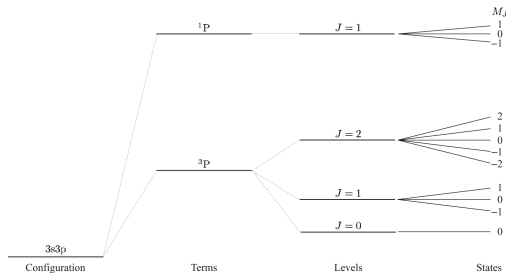Figure: Na $3^2P_{3/2} \to 3^2S_{1/2}$/ $3^2P_{1/2} \to 3^2S_{1/2}$

Figure: The hierarchy of atomic structure for the 3s3p configuration of an alkaline earth metal atom.

Break down:
(a) The residual electrostatic interaction is not small compared to the energy gap between the configurations.
(b) The jj-coupling scheme is a better approximation than LS-coupling.
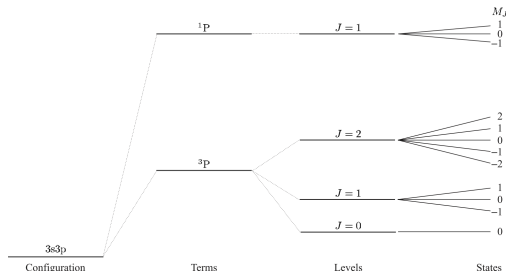(c) The Paschen–Back effect arises.

Figure: The hierarchy of atomic structure for the 3s3p configuration of an alkaline earth metal atom.

Break down:

(a) The residual electrostatic interaction is not small compared to the energy gap between the configurations.

(b) The jj-coupling scheme is a better approximation than LS-coupling.

(c) The Paschen–Back effect arises.

Reference

📄 C. Foot, *Atomic Physics*. Oxford University Press, 2005.

📄 赵凯华，罗蔚茵, 新概念物理教程 · 量子物理. 高等教育出版社, 2007.

📄 刘玉鑫，曹庆宏编著, 量子力学. 科学出版社, 2023.

Q&A

Thank you for listening!