The LS-coupling scheme

Atomic Physics Chapter 5

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Content

Hamiltonian

The central-field approximation

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

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

The residual electrostatic interaction：

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

Hamiltonian:

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

Hamiltonian

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

Hamiltonian

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

1. LS-coupling scheme:

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

2. jj-coupling scheme:

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

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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:

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

H_{re} doesn't depend on spin:

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LS-coupling scheme without fine structu

Therefore,

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

Label:

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

e.g. 3p4p in silicon

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

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Energy levels

Isotropy: degeneracy with respect to M_L and M_S.

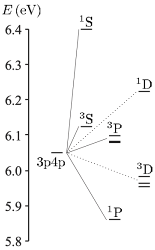

Figure: 3p4p in silicon

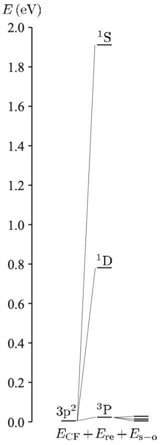

Figure: $3p^2$ in silicon

Degenerate states

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

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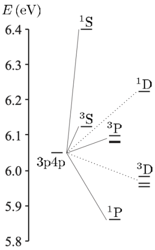

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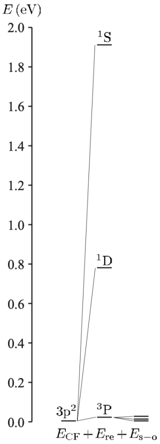

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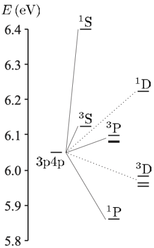

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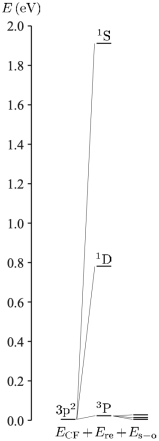

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Fine structure in the LS-coupling scheme

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: $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$.

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

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Fine structure in the LS-coupling scheme

Therefore, L_z, S_z are no longer conserved.

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

The energy shift: (degeneracy with respect to M_J)

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

Lande interval rule

The energy interval between adjacent J levels:

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

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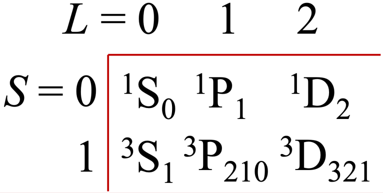
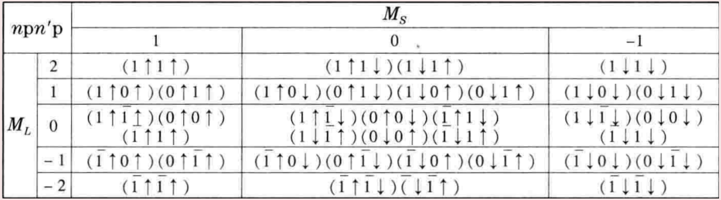
Example: pp electronic configuration

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



	$L=0$	1	2
$S=0$	$^1S_0$	$^1P_1$	$^1D_2$
1	$^3S_1$	$^3P_{210}$	$^3D_{321}$



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

[a]

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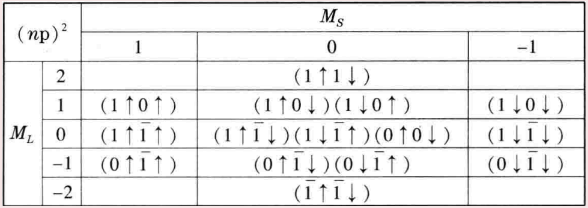
[a] $\bar{1} = -1.$

Example: pp electronic configuration

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

For equivalent electrons the Pauli exclusion principle restricts the states.



$(np)^2$		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:

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

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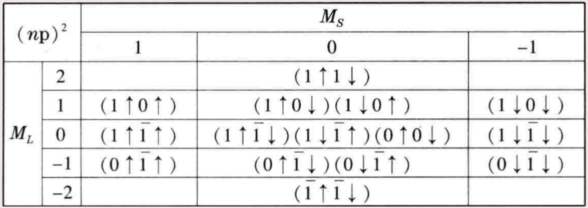

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	−1	$(0\uparrow \bar{1}\uparrow)$	$(0\uparrow \bar{1}\downarrow)(0\downarrow \bar{1}\uparrow)$	$(0\downarrow \bar{1}\downarrow)$
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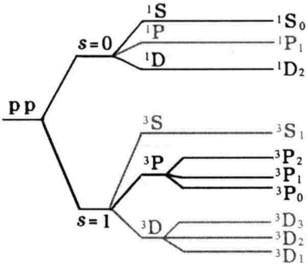


Figure: pp electronic configuration energy levels

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

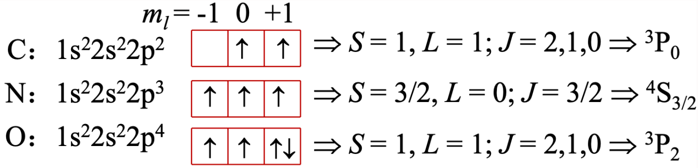
Hund's rules

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



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

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

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

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

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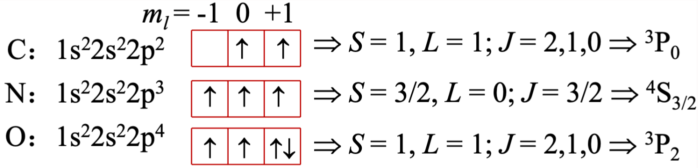

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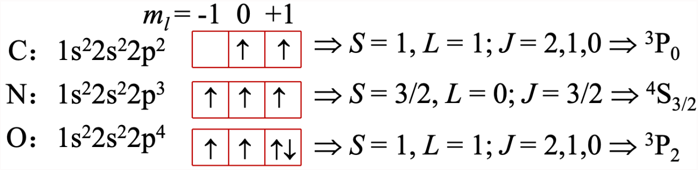

	$m_l =$	-1	0	+1	
C:	$1s^22s^22p^2$		↑	↑	$\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_0$
N:	$1s^22s^22p^3$	↑	↑	↑	$\Rightarrow S = 3/2, L = 0; J = 3/2 \Rightarrow {}^4S_{3/2}$
O:	$1s^22s^22p^4$	↑	↑	↑↓	$\Rightarrow S = 1, L = 1; J = 2,1,0 \Rightarrow {}^3P_2$

Hund's rules

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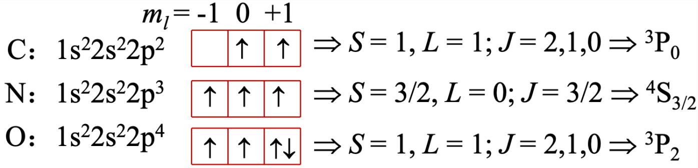

		$m_l =$ -1	0	+1	
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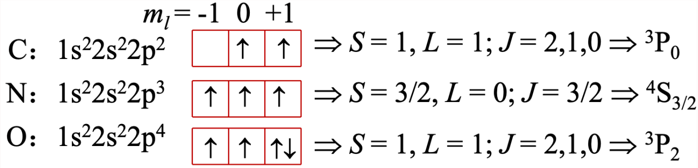

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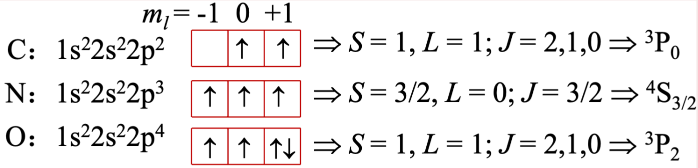

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Theoretical explanation

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:

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

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Content

The jj-coupling scheme

Hamiltonian

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

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

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

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

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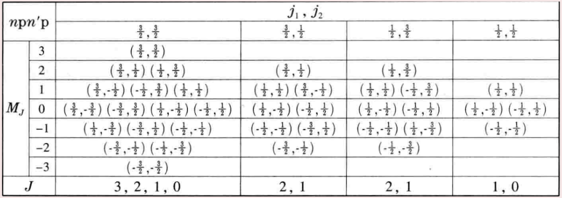
Example: pp electronic configuration

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



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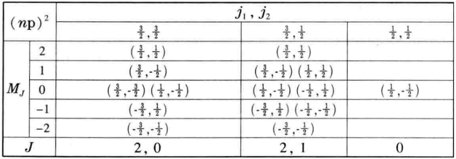
	−1	$(\frac{1}{2},-\frac{3}{2})$ $(-\frac{3}{2},\frac{1}{2})$ $(-\frac{1}{2},-\frac{1}{2})$	$(-\frac{1}{2},-\frac{1}{2})$ $(-\frac{3}{2},\frac{1}{2})$	$(-\frac{1}{2},-\frac{1}{2})$ $(\frac{1}{2},-\frac{3}{2})$	$(-\frac{1}{2},-\frac{1}{2})$
	−2	$(-\frac{3}{2},-\frac{1}{2})$ $(-\frac{1}{2},-\frac{3}{2})$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

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

For equivalent electrons the Pauli exclusion principle restricts the states.



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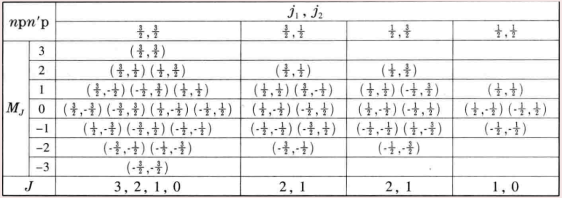

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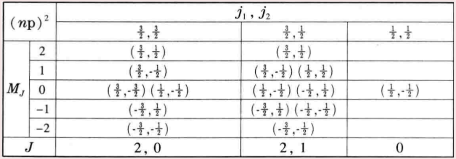

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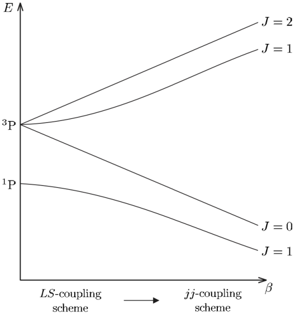
Content

In theory



[1]

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.

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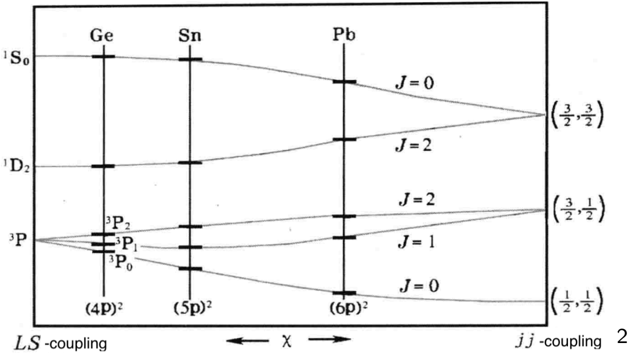
[1] β: the spin–orbit interaction parameter.

In theory and experiment



[2]

Figure: p^2 configuration

A evident transition by χ.

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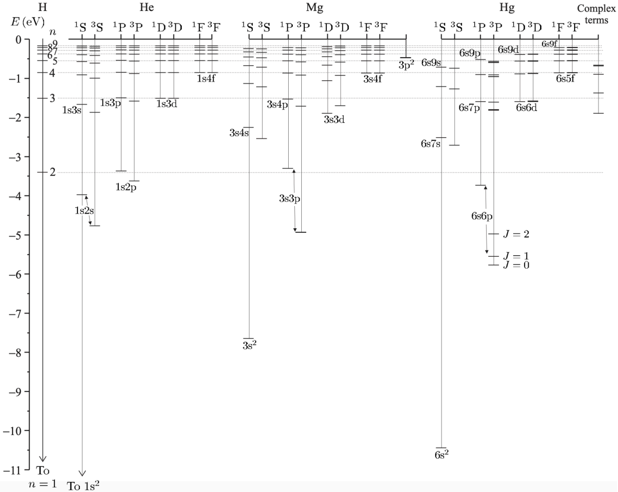
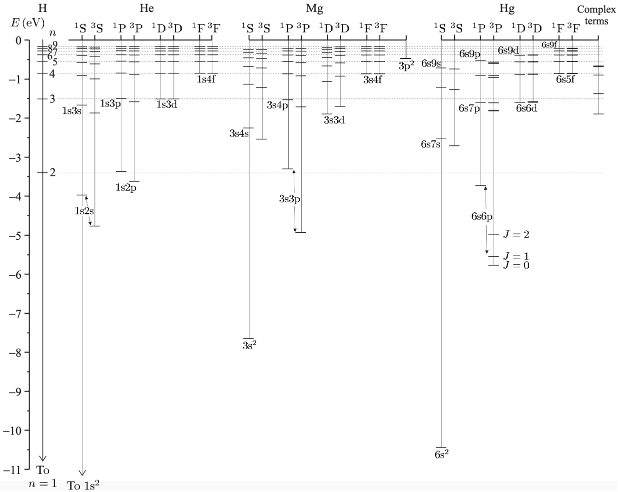
[2] χ: characteristic parameter.

In experiment



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

In experiment



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

Table: E/m^{-1}

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

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.

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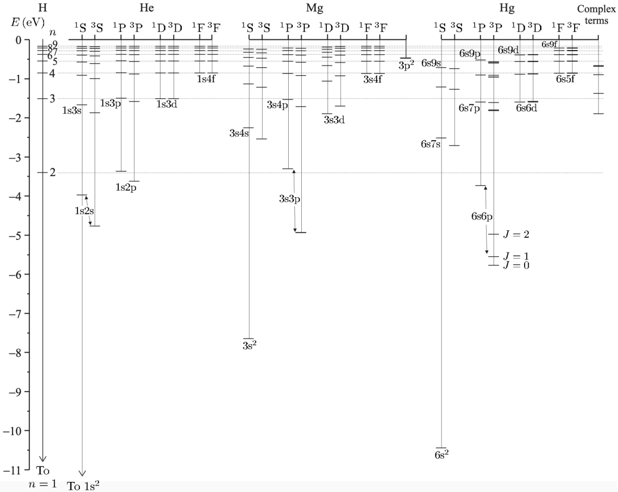

Even for Hg, the LS-coupling scheme gives a closer approximation than the jj-coupling scheme.

J	$E\ (\mathrm{m}^{-1})$
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.

Content

Electric dipole selection rules

Single electron

From conservation laws and quantum mechanics calculations:

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

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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.

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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:

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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:

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

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Example

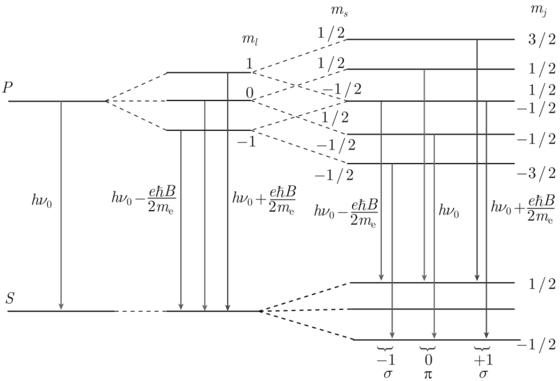

Figure: $m_l = 1, m_s = -\frac{1}{2}, m_j = \frac{1}{2} \& m_l = -1, m_s = \frac{1}{2}, m_j = -\frac{1}{2}$ are degenerate

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:

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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 $g_s \simeq 2$:

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

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

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:

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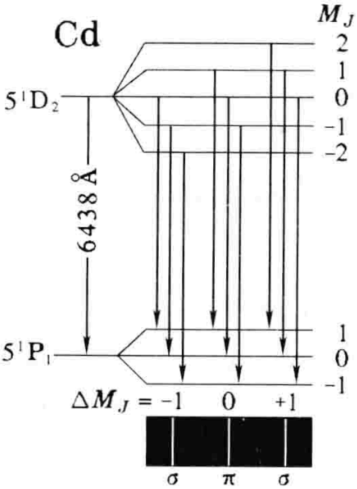

Figure: Cd $5^1\mathrm{D}_2 \to 5^1\mathrm{P}_1$: $S_1 = S_2 = 0 \Rightarrow g_1 = g_2 = 1$

The anomalous Zeeman effect

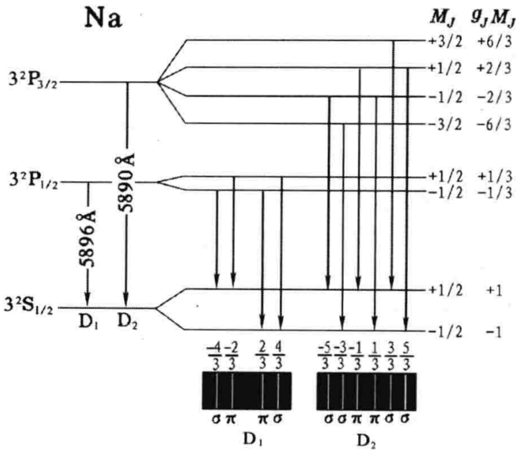

Figure: Na $3^2P_{3/2} \rightarrow 3^2S_{1/2}$/ $3^2P_{1/2} \rightarrow 3^2S_{1/2}$

Content

Summary

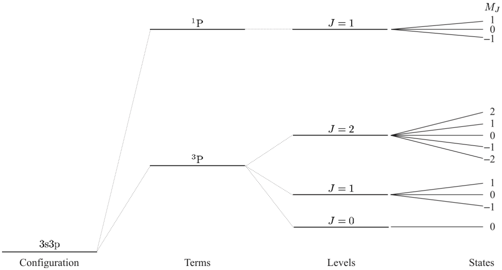

Figure: The hierarchy of atomic structure for the 3s3p configuration of an alkaline earth metal atom.

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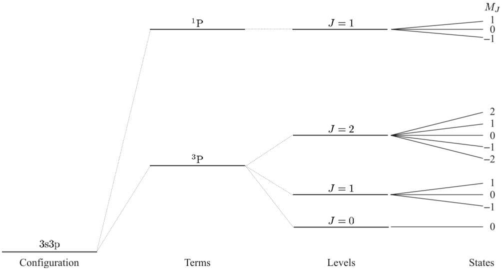

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- 刘玉鑫，曹庆宏编著, 量子力学. 科学出版社, 2023.

Q&A

Thank you for listening!