two - electron case :

Table 17.2. Transformation properties of two-electron states under permutations

configuration	state	irreducible representations	allowed states
$(\alpha_1\beta_2 - \beta_1\alpha_2)/\sqrt{2}$	$S=0$	Γ_1^a	
$(\alpha_1\alpha_2 + \alpha_2\alpha_1)/\sqrt{2}, \ldots$	$S=1$	Γ_1^s	
s^2	$L=0$	Γ_1^s	^1S
$1s2s$	$L=0$	$\Gamma_1^s + \Gamma_1^a$	^1S, ^3S
sp	$L=1$	$\Gamma_1^s + \Gamma_1^a$	^1P, ^3P
p^2	$L=0$	Γ_1^s	^1S
p^2	$L=1$	Γ_1^a	^3P
p^2	$L=2$	Γ_1^s	^1D
pd	$L=1$	$\Gamma_1^s + \Gamma_1^a$	$^1P + {}^3P$
pd	$L=2$	$\Gamma_1^s + \Gamma_1^a$	$^1D + {}^3D$
pd	$L=3$	$\Gamma_1^s + \Gamma_1^a$	$^1F + {}^3F$
d^2	$L=0$	Γ_1^s	^1S
d^2	$L=1$	Γ_1^a	^3P
d^2	$L=2$	Γ_1^s	^1D
d^2	$L=3$	Γ_1^a	^3F
d^2	$L=4$	Γ_1^s	^1G
f^2	$L=0$	Γ_1^s	^1S
f^2	$L=1$	Γ_1^a	^3P
f^2	$L=2$	Γ_1^s	^1D
f^2	$L=3$	Γ_1^a	^3F
f^2	$L=4$	Γ_1^s	^1G
f^2	$L=5$	Γ_1^a	^3H
f^2	$L=6$	Γ_1^s	^1I

^{2S+1}L

The symmetries of the irreducible representations of the permutation group $P(2)$ label the various spin and orbital angular momentum states. To obtain states allowed by the Pauli Principle, the direct product of the symmetries between the orbital and spin states must contain Γ_1^a

Table 17.3. Extended character table for permutation group $P(3)$

	χ(E)	χ(A,B,C)	χ(D,F)	
$P(3)$	(1^3)	$3(2,1)$	$2(3)$	
Γ_1^s	1	1	1	
Γ_1^a	1	-1	1	
Γ_2	2	0	-1	
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_1)$	1	1	1	$\Rightarrow \Gamma_1^s$
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_2)$	3	1	0	$\Rightarrow \Gamma_1^s + \Gamma_2$
$\Gamma_{\text{perm.}}(\psi_1\psi_2\psi_3)$	6	0	0	$\Rightarrow \Gamma_1^s + \Gamma_1^a + 2\Gamma_2$

odd perm

even perm

作basis

重排

正规表示分解

A, B, C : odd permutation

(交换两个不变量)

2维表示、

一元三次方程的三个根两种不变量

对角元为0

特征根为0

以$|\Gamma_2\alpha\rangle = a + \omega b + \omega^2 c$，$|\Gamma_2\beta\rangle = a + \omega^2 b + \omega c$
为基，计算表示矩阵

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad B = \begin{pmatrix} 0 & \omega \\ \omega^2 & 0 \end{pmatrix}$$

$$C = \begin{pmatrix} 0 & \omega^2 \\ \omega & 0 \end{pmatrix} \quad D = \begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix} \quad F = \begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix}$$

$\chi(E) = 2$

$\chi(D) = \chi(F) = \omega + \omega^2 = -1$

$\chi(A) = \chi(B) = \chi(C) = 0$

Table 17.4. Transformation properties of three-electron states under permutations[(a)]

configuration	state	irreducible representation	allowed state
(↑↑↓)	$S = 1/2$	Γ_2 $+ \Gamma_1^s$	
(↑↑↑)	$S = 3/2$	Γ_1^s	
s^3	$L = 0$	Γ_1^s	–
$1s^2 2s$	$L = 0$	$\Gamma_1^s + \Gamma_2$	^2S
$s^2 p$	$L = 1$	$\Gamma_1^s + \Gamma_2$	^2P
sp^2	$L = 0$	$\Gamma_1^s + \Gamma_2$	^2S
sp^2	$L = 1$	$\Gamma_1^a + \Gamma_2$	^2P, ^4P
sp^2	$L = 2$	$\Gamma_1^s + \Gamma_2$	^2D
$(2p)^2(3p)$	$L = 0$	$\Gamma_1^a + \Gamma_2$	^2S, ^4S
$(2p)^2(3p)$	$L = 1$	$2\Gamma_1^s + \Gamma_1^a + 3\Gamma_2$	^2P, ^2P, ^2P, ^4P
$(2p)^2(3p)$	$L = 2$	$\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$	^2D, ^2D, ^4D
$(2p)^2(3p)$	$L = 3$	$\Gamma_1^s + \Gamma_2$	^2F
p^3	$L = 0$	Γ_1^a	^4S
p^3	$L = 1$	$\Gamma_1^s + \Gamma_2$	^2P
p^3	$L = 2$	Γ_2	^2D
p^3	$L = 3$	Γ_1^s	–
d^3	$L = 0$	Γ_1^s	–
d^3	$L = 1$	$\Gamma_1^a + \Gamma_2$	^2P, ^4P
d^3	$L = 2$	$\Gamma_1^s + 2\Gamma_2$	^2D, ^2D
d^3	$L = 3$	$\Gamma_1^s + \Gamma_1^a + \Gamma_2$	^2F, ^4F
d^3	$L = 4$	$\Gamma_1^s + \Gamma_2$	^2G
d^3	$L = 5$	Γ_2	^2H
d^3	$L = 6$	Γ_1^s	–
f^3	$L = 0$	Γ_1^a	^4S
f^3	$L = 1$	$\Gamma_1^s + \Gamma_2$	^2P
f^3	$L = 2$	$\Gamma_1^a + 2\Gamma_2$	^2D, ^2D, ^4D
f^3	$L = 3$	$2\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$	^2F, ^2F, ^4F
f^3	$L = 4$	$\Gamma_1^s + \Gamma_1^a + 2\Gamma_2$	^2G, ^2G, ^4G
f^3	$L = 5$	$\Gamma_1^s + 2\Gamma_2$	^2H, ^2H
f^3	$L = 6$	$\Gamma_1^s + \Gamma_1^a + \Gamma_2$	^2I, ^4I
f^3	$L = 7$	$\Gamma_1^s + \Gamma_2$	^2J
f^3	$L = 8$	Γ_2	^2K
f^3	$L = 9$	Γ_1^s	–

$2S+1$ L

$S = \frac{1}{2}$

$L = 2$

[(a)] The symmetries of the irreducible representations of the permutation group $P(3)$ label the various spin and orbital angular momentum states. To obtain the states allowed by the Pauli Principle, the direct product of the symmetries between the orbital and spin states must contain Γ_1^a

Dressel haus : chap 17

三电子情形分析 Table 17.4

Table 17.4

sp^2 $L=2$ case (orbital)

两个p轨道 一个s ~ irreducible representation 一个3维表示约化为 $1 \oplus 2$ 两个不可约表示

$\Gamma_{perm}(\psi_1\psi_1\psi_2) = \Gamma_1^s + \Gamma_2$: orbital part

ψ_1 : p 轨道

ψ_2 : s 轨道

$\otimes$ $\underline{\Gamma_2}(\uparrow\uparrow\downarrow)^{s=\frac{1}{2}}$: spin part

(unique choice for this case)

in total : Γ_2 $(S=\frac{1}{2})$ & Γ_1^s $(S=\frac{3}{2})$ $\uparrow\uparrow\uparrow$ $\psi_1\psi_1\psi_1$

$\otimes$ $(\Gamma_1^s + \Gamma_2)$

Can not satisfy pauli principle

只有 $\Gamma_2 \otimes (\Gamma_1^s + \Gamma_2)$

可以

Table 17.3. Extended character table for permutation group $P(3)$

	$\chi(E)$	$\chi(A,B,C)$	$\chi(D,F)$	
$P(3)$ (1)(2)(3)	(1^3) (12)(3)	$3(2,1)$	$2(3)$ (123)	
Γ_1^s	1	1	1	
Γ_1^a	1	-1	1	
Γ_2	2	0	-1	
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_1)$	1	1	1	$\Rightarrow \Gamma_1^s$
$\Gamma_{\text{perm.}}(\psi_1\psi_1\psi_2)$	3	1	0	$\Rightarrow \Gamma_1^s + \Gamma_2$
$\Gamma_{\text{perm.}}(\psi_1\psi_2\psi_3)$	6	0	0	$\Rightarrow \Gamma_1^s + \Gamma_1^a + 2\Gamma_2$

leave one of the partners invariant

all partners vary

$$\chi^{\text{reducible}}(C_k) = \sum_{\Gamma_j} a_j \chi^{(\Gamma_j)}(C_k)$$

$$a_j = \frac{1}{h} \sum_k N_k \chi^{(\Gamma_j)}(C_k)^* \chi^{\text{reducible}}(C_k)$$

h ↓ group order

N_k ↓ # of elements in class k

$$\Gamma_1^s \otimes \Gamma_2 = \Gamma_2$$

$$a_{\Gamma_1^s} = \frac{1}{6}[1\times1\times2 + 3\times1\times0 + 2\times1\times(-1)] = 0$$

$$a_{\Gamma_1^a} = \frac{1}{6}[1\times1\times2 + 3\times(-1)\times0 + 2\times1\times(-1)] = 0$$

$$a_{\Gamma_2} = \frac{1}{6}[1\times2\times2 + 3\times0\times0 + 2\times(-1)\times(-1)] = 1$$

$$\Gamma_2 \otimes \Gamma_2 = \Gamma_1^s + \Gamma_1^a + \Gamma_2$$

the direct product of

the symmetries between the orbital and

spin states must contain Γ_1^a

Q: Γ_2 is symmetric representation ?

orbital part s p p

spin ↑ ↑ ↓

（三个电子，两种选择）

在置换意义下 spin / orbital 相同，

都是表 17.3 中 $\Gamma_{perm}(\psi_1\psi_1\psi_2)$

所以 $(\Gamma_1^s + \Gamma_2) \otimes (\Gamma_1^s + \Gamma_2)$

$\Gamma_1^s \otimes (\Gamma_1^s + \Gamma_2)$ 分离不出 Γ_1^a

↑↑↑ configuration 不可选

$\Gamma_2 \otimes (\Gamma_1^s + \Gamma_2)$

可约表示，特征标分解公式

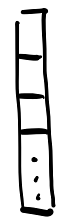
$$\chi^{\text{reducible}}(C_k) = \sum_{\Gamma_j} a_j \chi^{(\Gamma_j)}(C_k)$$

$$a_j = \frac{1}{h} \sum_k N_k \chi^{(\Gamma_j)}(C_k)^* \chi^{\text{reducible}}(C_k)$$

h ↓ group order

N_k ↓ # of elements in class k

这个题真不简单： Γ_1^n 是一维的全反称表示



仔细阅读 see 17.3 (P437 ~)

Dresselhaus

全反称算符为 $\hat{A} = \sum(\text{even perm} \overset{(-1)}{-} \text{odd perm})$

$$\hat{A} = \sum_{q \in C(T)} \delta_q \hat{q}$$

C : column　　Table中的列置换

R : Row

$\delta_q = 1$: $\hat{q}$ 为 even perm

$= -1$, $\hat{q}$ 为 odd ~

spin

Γ_1^s ($\uparrow\uparrow\uparrow$)　$\otimes$　$(\varphi_1 \varphi_1 \varphi_2)$　会出现两个电子占据相同的 spin & orbit 违背 pauli exclusion principle.

atomic number — 28

Ground-state level — $^{3}F_{4}$

symbol — Ni

name — Nickel

atomic weight — 58.6934

Ground-state configuration — [Ar] $3d^8 4s^2$

7.6399 — Ionization energy (eV)

$^{2S+1}X_J$

$S = 1$, $L = 3$

here, $J = L + S$

electron mass m_e 9.1×10^{-31} kg

$m_e c^2$ 0.511 MeV

$L =$ 0 1 2 3 4 5 6

$X =$ S P D F G H I

nickel is a transition metal with unpaired electrons that can give rise to magnetic behavior.

讲了电子之前要讲直积群的表示，是群表示的直积，才有表示直积分解的问题，

顺便讲下4阶 Cyclic group

Klein group 表示问题

参见 chap 2 末尾

Cyclic

	E	A	A^2	A^3
D^1	1	1	1	1
D^2	1	i	-1	$-i$
D^3	1	-1	1	-1
D^4	1	$-i$	-1	i

Klein $= (C_2, i)$

inversion ↑

	E	C_2	i	σ_h	
D^1	1	1	1	1	$1\otimes 1$
D^2	1	1	-1	-1	$1\otimes 2$
D^3	1	-1	1	-1	$2\otimes 1$
D^4	1	-1	-1	1	$2\otimes 2$

接下来介绍 A_n

alternating group

S_n 的不变子群

以及 Cayley theorem ＋ 正则表示、