Configuration State Function (CSF)

2018.11.23

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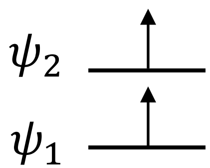
内容

- 背景
- CSF
- CSF与Slater行列式的转换
- 组态空间的产生
- 附录

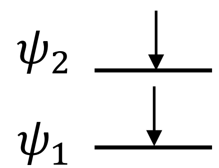
背景

对He原子，第一激发态的电子排布有如下4种



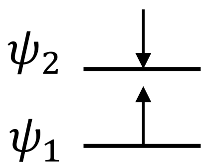
$$\frac{1}{\sqrt{2}}\begin{vmatrix}\psi_1(1)\alpha(1) & \psi_2(1)\alpha(1)\\ \psi_1(2)\alpha(2) & \psi_2(2)\alpha(2)\end{vmatrix}$$

$$\frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2)-\psi_1(2)\psi_2(1)]\alpha(1)\alpha(2)$$



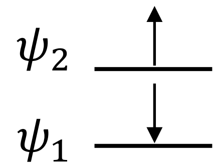
$$\frac{1}{\sqrt{2}}\begin{vmatrix}\psi_1(1)\beta(1) & \psi_2(1)\beta(1)\\ \psi_1(2)\beta(2) & \psi_2(2)\beta(2)\end{vmatrix}$$

$$\frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2)-\psi_1(2)\psi_2(1)]\beta(1)\beta(2)$$



$$\frac{1}{\sqrt{2}}\begin{vmatrix}\psi_1(1)\alpha(1) & \psi_2(1)\beta(1)\\ \psi_1(2)\alpha(2) & \psi_2(2)\beta(2)\end{vmatrix}$$

$$\frac{1}{\sqrt{2}}\boxed{[\psi_1(1)\psi_2(2)\alpha(1)\beta(2) - \psi_1(2)\psi_2(1)\alpha(2)\beta(1)]}$$



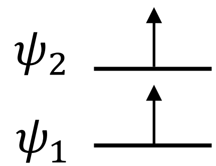
$$\frac{1}{\sqrt{2}}\begin{vmatrix}\psi_1(1)\beta(1) & \psi_2(1)\alpha(1)\\ \psi_1(2)\beta(2) & \psi_2(2)\alpha(2)\end{vmatrix}$$

$$\frac{1}{\sqrt{2}}\boxed{[\psi_1(1)\psi_2(2)\alpha(2)\beta(1) - \psi_1(2)\psi_2(1)\alpha(1)\beta(2)]}$$

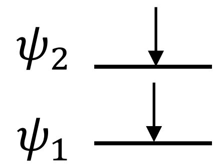
自旋部分与空间部分波函数不分离，需要线性组合

背景

$$\Psi_1 = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)]\alpha(1)\alpha(2)$$

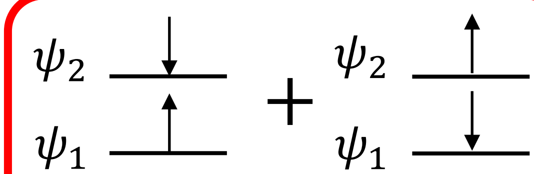


$$\Psi_2 = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)]\beta(1)\beta(2)$$

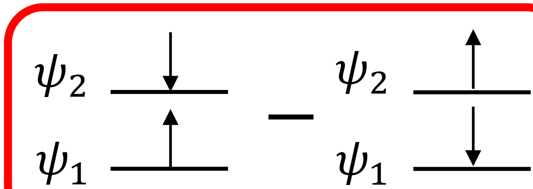


可将Slater行列式线性组合得到$\hat{S}^2$与$\hat{S}_z$共同的本征波函数

$$\Psi_3 = \frac{1}{2}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$



$$\Psi_4 = \frac{1}{2}[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$



三重态(^{3}S)：Ψ_1, Ψ_2, Ψ_3　$M_S = 1, -1, 0$　　$S = 1$

单重态(^{1}S)：Ψ_4　$M_S = 0$　　$S = 0$

Slater行列式是$\hat{S}_z$的本征波函数，不一定是$\hat{S}^2$的本征波函数

CSF

- Slater行列式的线性组合

$$|CSF\rangle = \sum_n c_n |det\rangle_n$$

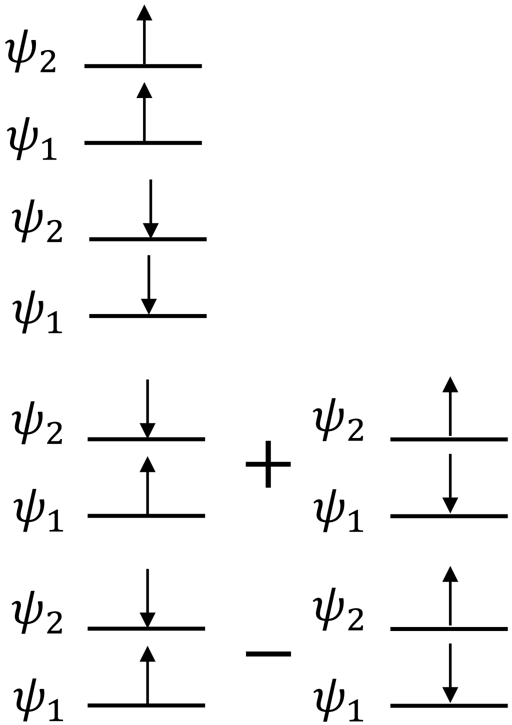
- $\hat{S}^2$的本征波函数

$$\hat{S}^2|CSF\rangle = \hbar S(S+1)|CSF\rangle$$

- $\hat{S}_z$的本征波函数

$$\hat{S}_z|CSF\rangle = \hbar M_s|CSF\rangle$$

CSF的表示



		①	②	③
$S=1$	$M_S=1$	$\|\frac{1}{2},1\rangle$	$\|uu\rangle$	$\|11\rangle$
$S=1$	$M_S=-1$	$\|\frac{1}{2},1\rangle$	$\|uu\rangle$	$\|11\rangle$
$S=1$	$M_S=0$	$\|\frac{1}{2},1\rangle$	$\|uu\rangle$	$\|11\rangle$
$S=0$	$M_S=0$	$\|\frac{1}{2},0\rangle$	$\|ud\rangle$	$\|12\rangle$

① 第n个数字表示第n个空间轨道上的电子加入体系后体系的S值

②③ 第n个数字表示该空间轨道上的电子加入体系后对体系S的影响

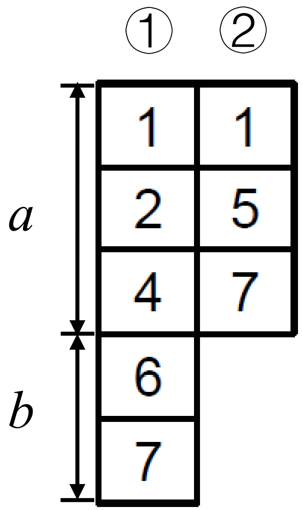
② 2: 轨道上有2个电子　u: 轨道上有1个使S增大的电子
d: 轨道上有1个使S减小的电子　0: 轨道上无电子

③ 0: 轨道上无电子　1: 轨道上有1个使S增大的电子
2: 轨道上有1个使S减小的电子　3: 轨道上有2个电子

一个CSF可能对应一种电子排布，也可能是几种电子排布的线性组合

CSF的表示

$|3101213\rangle$



$$[p] = \left|\begin{matrix} 3 & 2 & 2 \\ 2 & 2 & 2 \\ 2 & 1 & 2 \\ 1 & 2 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 0 \end{matrix}\right\rangle \quad d = \begin{pmatrix} 3 \\ 1 \\ 2 \\ 1 \\ 0 \\ 1 \\ 3 \end{pmatrix}$$

方块	电子
数字	电子所在空间轨道
①列	其中的电子使体系总自旋增大
②列	其中的电子使体系总自旋减小
a	图中含有①②列的行数
b	图中含有①列的行数

总电子数 $N = 2a + b$

总轨道数 $n = a + b + c$

总自旋 $S = \frac{1}{2}b$

Paldus盘（ABC盘） 步矢

$$[p] = \left|\begin{matrix} a_n & b_n & c_n \\ a_{n-1} & b_{n-1} & c_{n-1} \\ \cdots & \cdots & \cdots \\ a_1 & b_1 & c_1 \end{matrix}\right\rangle \quad d = \begin{pmatrix} d_n \\ d_{n-1} \\ \cdots \\ d_1 \end{pmatrix}$$

第k行强调了前k个轨道上的N_k个电子

构成自旋量子数S_k时的累加结果，且

$$a_k + b_k + c_k = k$$

$$x_k \geq 0 \ (x = a, b, c)$$

CSF的表示

Paldus盘（ABC盘）

$$[p] = \left| \begin{matrix} a_n & b_n & c_n \\ a_{n-1} & b_{n-1} & c_{n-1} \\ \cdots & \cdots & \cdots \\ a_1 & b_1 & c_1 \end{matrix} \right\rangle$$

步矢

$$d = \begin{pmatrix} d_n \\ d_{n-1} \\ \cdots \\ d_1 \end{pmatrix}$$

$$\Delta a_k + \Delta b_k + \Delta c_k = 1$$

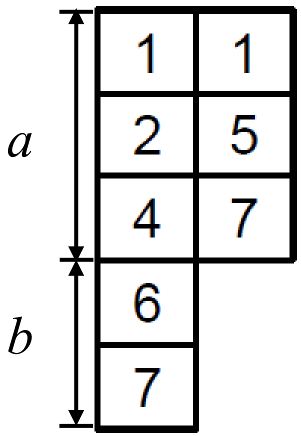
$$d_k = 3\Delta a_k + \Delta b_k$$

$$d_k = \frac{3}{2}\Delta N_k - \Delta S_k$$

$$\Delta x_k = x_k - x_{k-1} (x = a, b, c, N, S)$$

d_k	Δa_k	Δb_k	Δc_k	ΔN_k	ΔS_k	d_k的取值对应4种情况
0	0	0	1	0	0	轨道k上无电子
1	0	1	0	1	1/2	轨道k上有1个使体系总自旋增加的电子
2	1	-1	1	1	-1/2	轨道k上有1个使体系总自旋减少的电子
3	1	0	0	2	0	轨道k上有2个电子

CSF的表示



$N = 8, n = 7, S = 1$

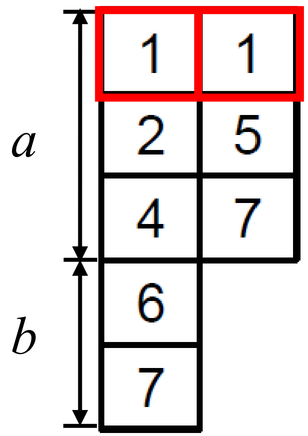
k	a	b	c	d
7				
6				
5				
4				
3				
2				
1				
0	0	0	0	-

总电子数 $N = 2a + b$

总轨道数 $n = a + b + c$

总自旋 $S = \frac{1}{2}b$

CSF的表示

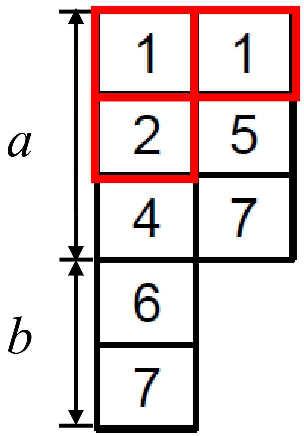


总电子数 $N = 2a + b$
总轨道数 $n = a + b + c$
总自旋 $S = \frac{1}{2}b$

$N = 8, n = 7, S = 1$

k	a	b	c	d
7				
6				
5				
4				
3				
2				
1	1	0	0	3
0	0	0	0	-

CSF的表示



$N = 8, n = 7, S = 1$

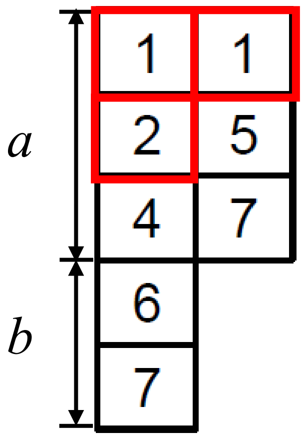
k	a	b	c	d
7				
6				
5				
4				
3				
2	1	1	0	1
1	1	0	0	3
0	0	0	0	-

总电子数 $N = 2a + b$

总轨道数 $n = a + b + c$

总自旋 $S = \frac{1}{2}b$

CSF的表示



$N = 8, n = 7, S = 1$

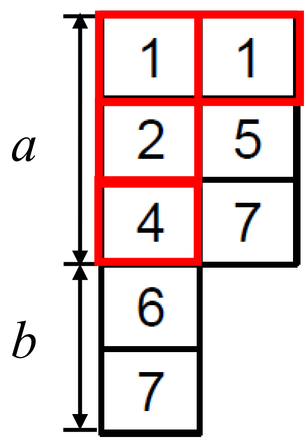
k	a	b	c	d
7				
6				
5				
4				
3	1	1	1	0
2	1	1	0	1
1	1	0	0	3
0	0	0	0	-

总电子数 $N = 2a + b$

总轨道数 $n = a + b + c$

总自旋 $S = \frac{1}{2}b$

CSF的表示



总电子数 $N = 2a + b$

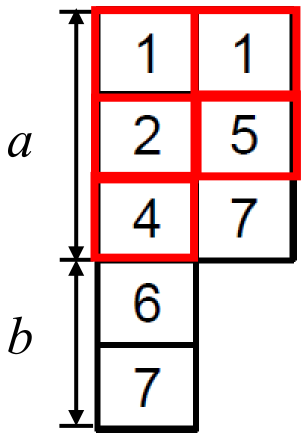
总轨道数 $n = a + b + c$

总自旋 $S = \frac{1}{2}b$

$N = 8, n = 7, S = 1$

k	a	b	c	d
7				
6				
5				
4	1	2	1	1
3	1	1	1	0
2	1	1	0	1
1	1	0	0	3
0	0	0	0	-

CSF的表示



$N = 8, n = 7, S = 1$

k	a	b	c	d
7				
6				
5	2	1	2	2
4	1	2	1	1
3	1	1	1	0
2	1	1	0	1
1	1	0	0	3
0	0	0	0	-

总电子数 $N = 2a + b$

总轨道数 $n = a + b + c$

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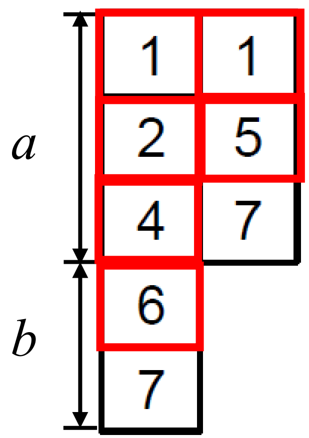
CSF的表示



总电子数 $N = 2a + b$

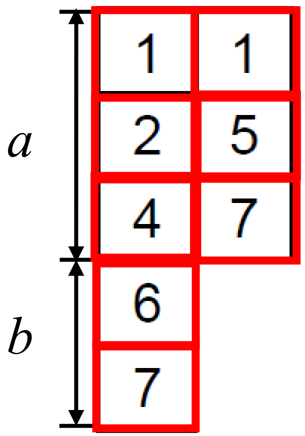
总轨道数 $n = a + b + c$

总自旋 $S = \frac{1}{2}b$

$N = 8, n = 7, S = 1$

k	a	b	c	d
7				
6	2	2	2	1
5	2	1	2	2
4	1	2	1	1
3	1	1	1	0
2	1	1	0	1
1	1	0	0	3
0	0	0	0	-

CSF的表示



$N = 8, n = 7, S = 1$

k	a	b	c	d
7	3	2	2	3
6	2	2	2	1
5	2	1	2	2
4	1	2	1	1
3	1	1	1	0
2	1	1	0	1
1	1	0	0	3
0	0	0	0	-

总电子数 $N = 2a + b$

总轨道数 $n = a + b + c$

总自旋 $S = \frac{1}{2}b$

CSF与Slater行列式的转换

1. 确定体系总电子数N，总空间轨道数n，总自旋量子数S，总自旋z分量量子数M_s
2. 对某个满足条件1的CSF，找出所有可以线性组合成该CSF的Slater行列式。
3. 所有Slater行列式除满足条件1外，还需满足：第k个空间轨道上的电子数与CSF的相同
4. 满足条件的Slater行列式根据下列公式计算其系数f

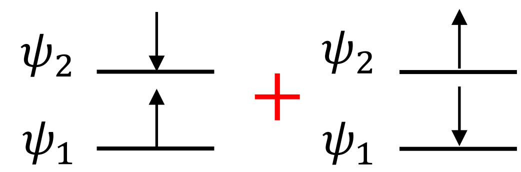
$$f = \prod_{k=1}^{n} f_k$$

$$
\begin{aligned}
f_k &= 1 && \text{if } d_k = 0 \\
f_k &= \sqrt{(a_k + b_k - \gamma_k)/b_k} && \text{if } d_k = 1 \\
f_k &= (-1)^{b_k+\delta_k}\sqrt{(\gamma_k - a_k + 1)/(b_k + 2)} && \text{if } d_k = 2 \\
f_k &= (-1)^{b_k} && \text{if } d_k = 3
\end{aligned}
$$

γ_k: 在Slater行列式的第k个空间轨道之前，与第k个空间轨道上的电子自旋相反的自旋轨道数

$\delta_k = 1$: 第k个轨道上为α电子

$\delta_k = 0$: 第k个轨道上为β电子



$N = 2, n = 2, S = 1, M_s = 0$

1
2

$|11\rangle$

k	a	b	c	d
2	0	2	0	1
1	0	1	0	1

	$\lvert 1\bar{2}\rangle_d$		$\lvert \bar{1}2\rangle_d$	
k	γ	δ	γ	δ
2	1	0	1	1
1	0	1	0	0

$$|11\rangle_c = \frac{1}{\sqrt{2}}|1\bar{2}\rangle_d + \frac{1}{\sqrt{2}}|\bar{1}2\rangle_d$$

CSF与Slater行列式的转换

1. 确定体系总电子数N，总空间轨道数n，总自旋量子数S，总自旋z分量量子数M_s
2. 对某个满足条件1的CSF，找出所有可以线性组合成该CSF的Slater行列式。
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4. 满足条件的Slater行列式根据下列公式计算其系数f

$$f = \prod_{k=1}^{n} f_k$$

$$f_k = 1 \qquad \text{if} \quad d_k = 0$$

$$f_k = \sqrt{(a_k + b_k - \gamma_k)/b_k} \qquad \text{if} \quad d_k = 1$$

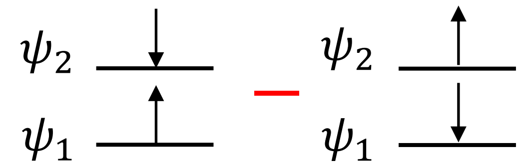
$$f_k = (-1)^{b_k+\delta_k}\sqrt{(\gamma_k - a_k + 1)/(b_k + 2)} \qquad \text{if} \quad d_k = 2$$

$$f_k = (-1)^{b_k} \qquad \text{if} \quad d_k = 3$$

γ_k: 在Slater行列式的第k个空间轨道之前，与第k个空间轨道上的电子自旋相反的自旋轨道数

$\delta_k = 1$: 第k个轨道上为α电子

$\delta_k = 0$: 第k个轨道上为β电子



$N = 2, n = 2, S = 0, M_s = 0$

1	2

$|12\rangle$

k	a	b	c	d
2	1	0	1	2
1	0	1	0	1

	$\lvert 1\bar{2}\rangle_d$		$\lvert \bar{1}2\rangle_d$	
k	γ	δ	γ	δ
2	1	0	1	1
1	0	1	0	0

$$|12\rangle_c = \frac{1}{\sqrt{2}}|1\bar{2}\rangle_d - \frac{1}{\sqrt{2}}|\bar{1}2\rangle_d$$

CSF与Slater行列式的转换

$$
\begin{aligned}
f_k &= 1 && \text{if} \quad d_k = 0 \\
f_k &= \sqrt{(a_k + b_k - \gamma_k)/b_k} && \text{if} \quad d_k = 1 \\
f_k &= (-1)^{b_k+\delta_k}\sqrt{(\gamma_k - a_k + 1)/(b_k + 2)} && \text{if} \quad d_k = 2 \\
f_k &= (-1)^{b_k} && \text{if} \quad d_k = 3
\end{aligned}
$$

γ_k: 在Slater行列式的第k个空间轨道之前，与第k个空间轨道上的电子自旋相反的自旋轨道数

$\delta_k = 1$: 第k个轨道上为α电子

$\delta_k = 0$: 第k个轨道上为β电子

k	a	b	c	d
7	2	1	4	2
6	1	2	3	0
5	1	2	2	0
4	1	2	1	1
3	1	1	1	3
2	0	1	1	0
1	0	1	0	1

1	3
3	7
4	

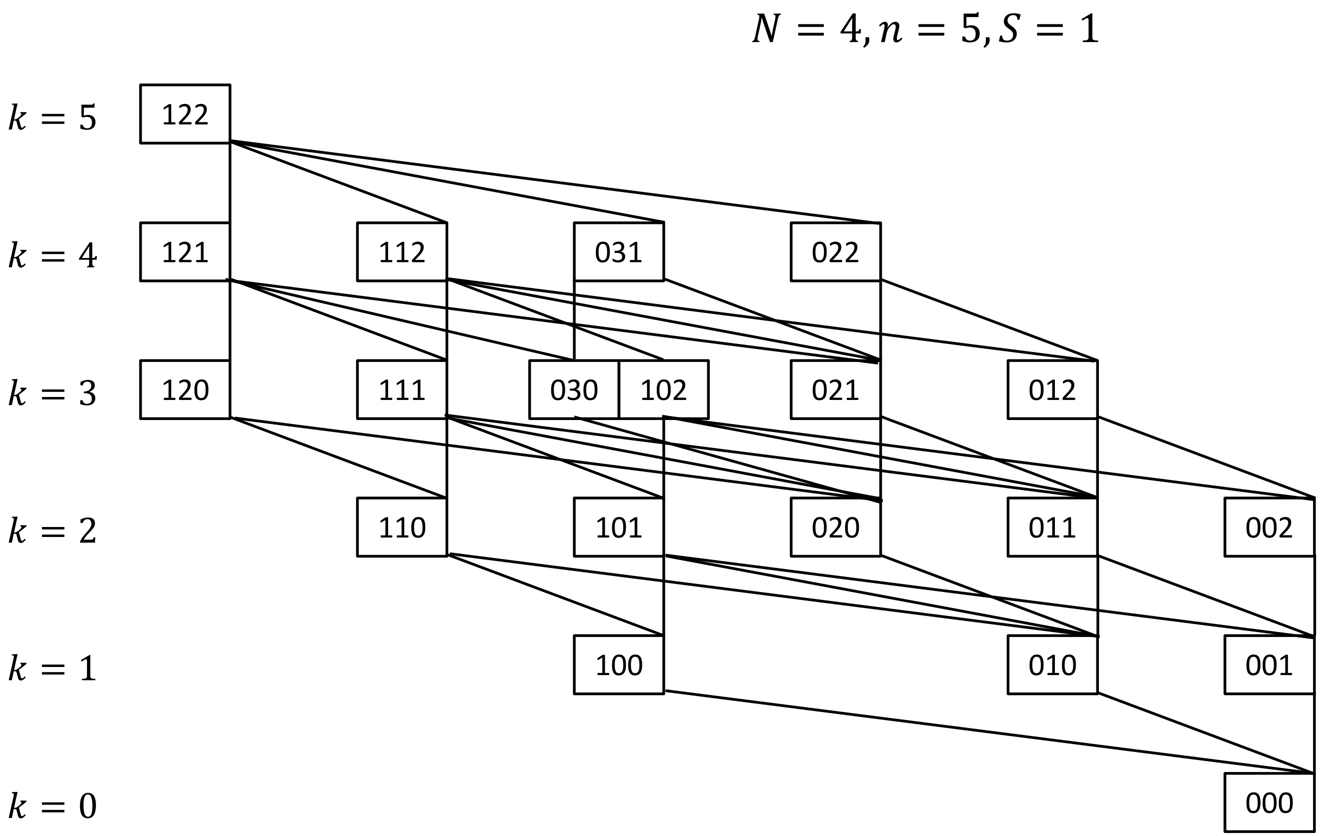
$|1031002\rangle$

$$N = 5, n = 7, S = \frac{1}{2}, M_s = \frac{1}{2}$$

$$|1031002\rangle_C = \frac{1}{\sqrt{6}}\left(2|133\bar{3}4\bar{7}\rangle_d - |\bar{1}3\bar{3}47\rangle_d - |13\bar{3}\bar{4}7\rangle_d\right)$$

	$\|\bar{1}3\bar{3}47\rangle_d$			$\|13\bar{3}\bar{4}7\rangle_d$			$\|13\bar{3}4\bar{7}\rangle_d$		
k	γ	δ	f	γ	δ	f	γ	δ	f
7	2	1	$\frac{1}{\sqrt{3}}$	2	1	$\frac{1}{\sqrt{3}}$	3	0	$\frac{-2}{\sqrt{6}}$
4	2	1	$\frac{1}{\sqrt{2}}$	2	0	$\frac{1}{\sqrt{2}}$	1	1	1
3	-	-	-1	-	-	-1	-	-	-1
1	0	0	1	0	1	1	0	1	1

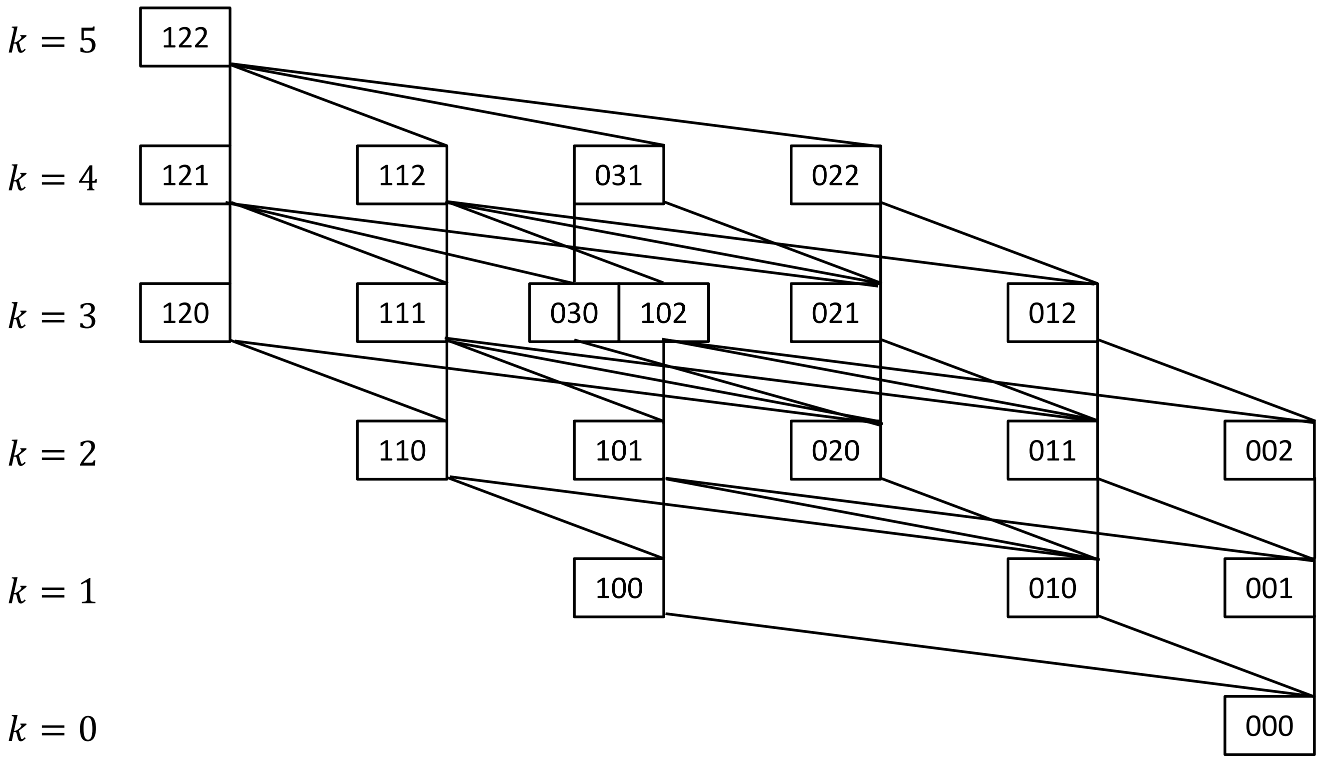
组态空间的产生



1. 纵向为轨道级，自上而下从大到小排列
2. 四种斜率不同的线段标记d_k
3. 各结点用其对应的$(a_k\ b_k\ c_k)$标记
4. 从图的顶行头结点(head)出发按d_k向下连接不同结点
5. 为使图形封闭，在最后一行增加一个尾结点(tail)
6. 从尾结点到头结点的任意一条线路表示一个CSF

组态空间的产生

$$N = 4, n = 5, S = 1$$



结点向下连接时不同d_k取值对应$(a_k\ b_k\ c_k)$的变化

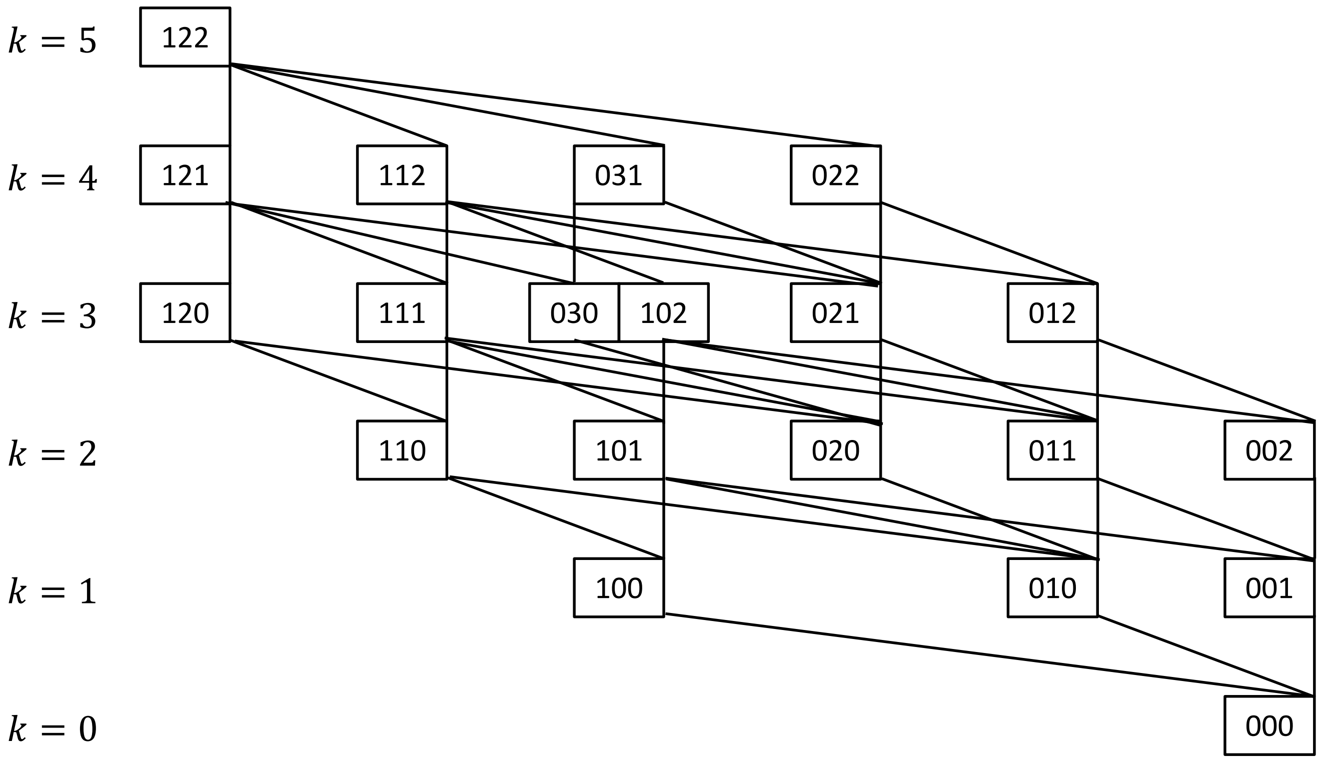
$d_k = 0$	$c_k - 1$
$d_k = 1$	$b_k - 1$
$d_k = 2$	$a_k - 1, c_k - 1$ $b_k + 1$
$d_k = 3$	$a_k - 1$

结点向下连接时的禁戒规则（保证$a_k, b_k, c_k \geq 0$）

结构特征	禁止步数
$a_k = 0$	$d_k = 2$ $d_k = 3$
$b_k = 0$	$d_k = 1$
$c_k = 0$	$d_k = 0$ $d_k = 2$

组态空间的产生

$N = 4, n = 5, S = 1$



结点向下连接时不同d_k取值对应$(a_k\ b_k\ c_k)$的变化

$d_k = 0$	$c_k - 1$
$d_k = 1$	$b_k - 1$
$d_k = 2$	$a_k - 1, c_k - 1$ $b_k + 1$
$d_k = 3$	$a_k - 1$

结点向下连接时的禁戒规则（保证$a_k, b_k, c_k \geq 0$）

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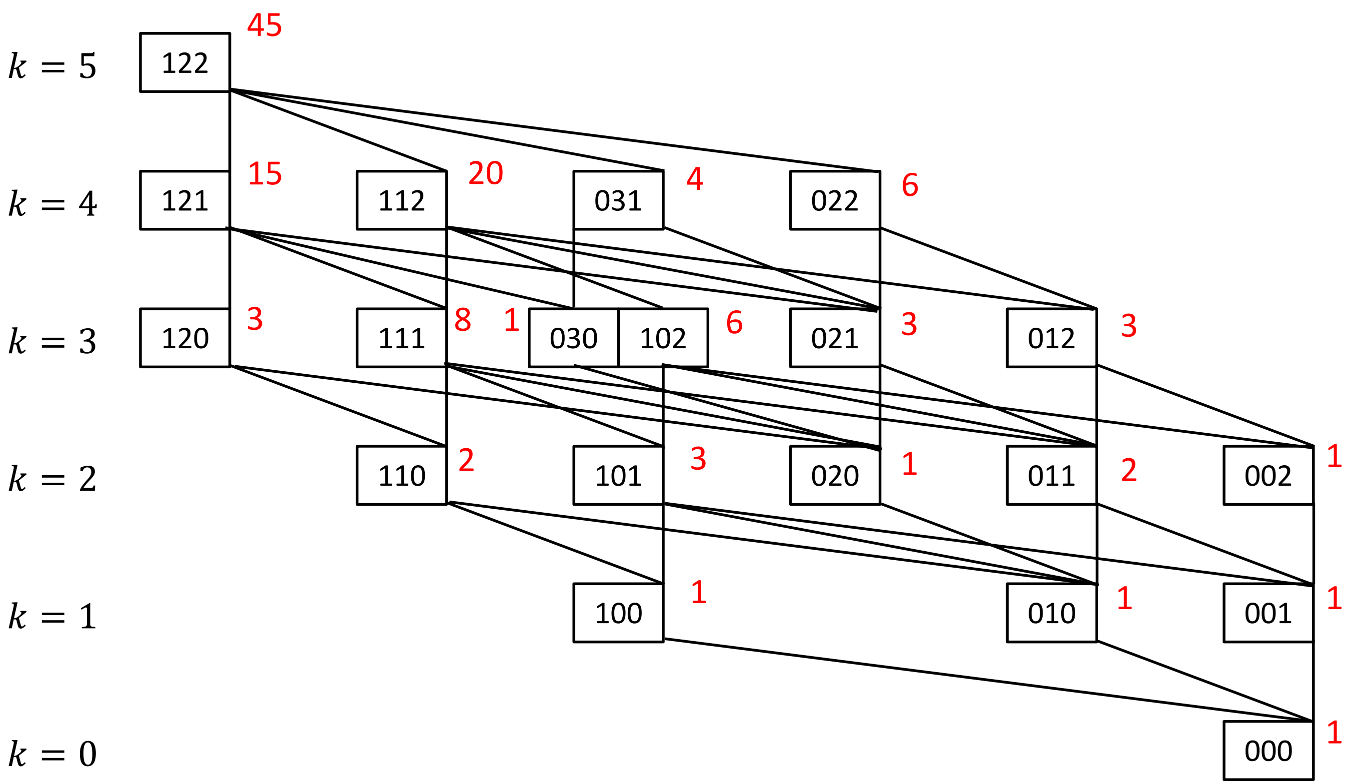
组态空间的产生

$N = 4, n = 5, S = 1$



每一结点赋予一个指标J，它是该结点在图中自上而下产生的顺序

结点权：结点J到尾的通道数

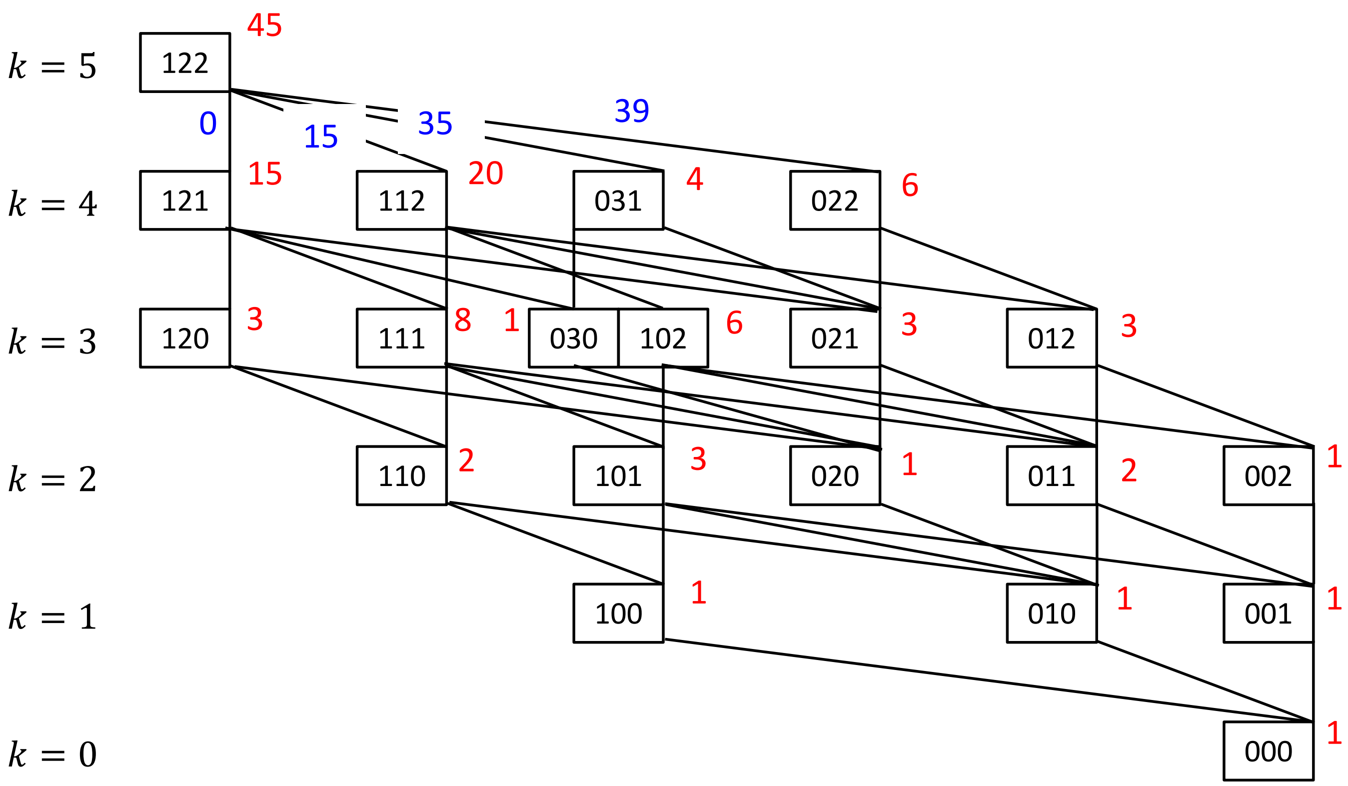
结点J的权等于与之相连的数个下结点$Jd_{\downarrow}$的权之和

$$X_J = \sum_{d=0}^{3} X_{Jd_{\downarrow}}$$

约定尾结点的权为1

头结点的权是图形从头到尾的通道数，即该图形所代表的组态数目

组态空间的产生



每一条连接两个结点的弧可以定义弧权

弧权：该弧上结点所连结的小于该弧步数(d')的下结点$Jd_{\downarrow}$的结点权之和，即$d < d'$的弧所连结的下结点的结点权之和，记为Y_{Jd}

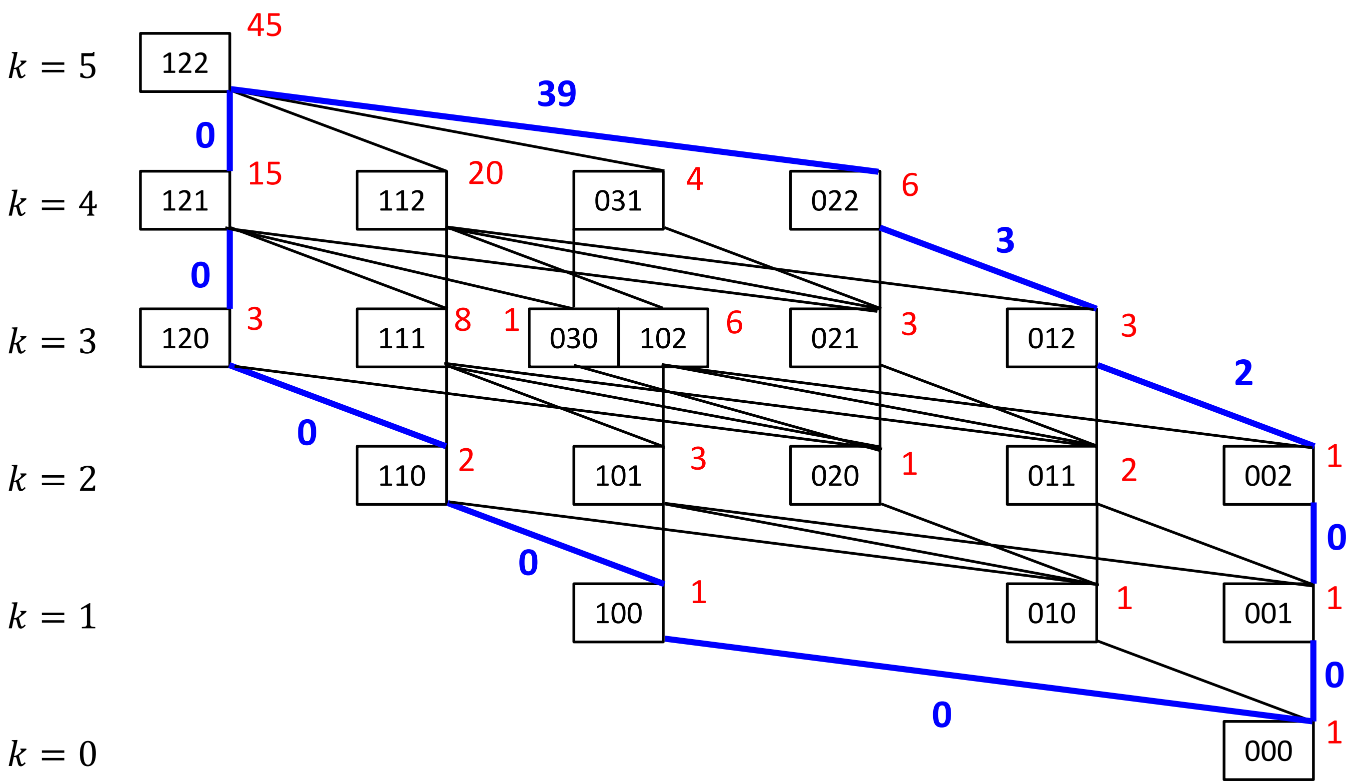
$$Y_{Jd} = \sum_{d'=0}^{d-1} X_{Jd'_{\downarrow}}$$

$$= Y_{Jd-1} + X_{Jd-1_{\downarrow}}$$

由定义，$Y_{J0} = 0$

组态空间的产生

$N = 4, n = 5, S = 1$



整步由n段弧连接而成，这些弧的弧权之和定义为该整步的步权，记作$W(d)$

$$W(d) = \sum_{k=1}^{n} (Y_{Jd})_k$$

利用步权可以给整步所代表的CSF赋予一种编序方式

组态的辞典顺序(Lexical)定义为步权加1

组态	步权	顺序
$\vert 31100\rangle$	0	1
$\vert 00113\rangle$	44	45

不同行表(Distinct Row Table, DRT)

J	k	a	b	c	$J0_{\downarrow}$	$J1_{\downarrow}$	$J2_{\downarrow}$	$J3_{\downarrow}$	$Y1$	$Y2$	$Y3$	X
1	5	1	2	2	2	3	4	5	15	35	39	45
2	4	1	2	1	6	7	8	10	3	11	12	15
3	4	1	1	2	7	9	10	11	8	14	17	20
4	4	0	3	1	8	10			1	0	0	4
5	4	0	2	2	10	11			3	0	0	6
6	3	1	2	0		12		14	0	0	2	3
7	3	1	1	1	12	13	14	15	2	5	6	8
8	3	0	3	0		13			0	0	0	1
9	3	1	0	2	13		15	16	0	3	5	6
10	3	0	2	1	14	15			1	0	0	3
11	3	0	1	2	15	16			2	0	0	3
12	2	1	1	0		17		18	0	0	1	2
13	2	1	0	1	17		18	19	0	1	2	3
14	2	0	2	0		18			0	0	0	1
15	2	0	1	1	18	19			1	0	0	2
16	2	0	0	2	19				0	0	0	0
17	1	1	0	0				20	0	0	0	1
18	1	0	1	0		20			0	0	0	1
19	1	0	0	1	20				0	0	0	1
20	0	0	0	0					0	0	0	1

参考文献

1. 文振翼，王育邠. 酉群方法的理论和应用. 上海科学技术出版社，1994
2. Isaiah Shavitt. The graphical unitary group approach and Its application to direct configuration interaction calculations.
3. Isaiah Shavitt. Graph Theoretical Concepts for the Unitary Group Approach to the Many-Electron Correlation Problem. International Journal of Quantum Chemistry: Quantum Chemistry Symposium 11, 131-148 (1977)

附录

- 类比角动量算符的性质，可定义自旋角动量算符
- $\hat{S}^2|s,m_s\rangle = \hbar^2 s(s+1)|s,m_s\rangle$
- $\hat{S}_z|s,m_s\rangle = \hbar m_s|s,m_s\rangle$
- $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$
- $\left[\hat{S}^2, \hat{S}_x\right] = \left[\hat{S}^2, \hat{S}_y\right] = \left[\hat{S}^2, \hat{S}_z\right] = 0$
- $\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z \quad \left[\hat{S}_y, \hat{S}_z\right] = i\hbar\hat{S}_x \qquad \left[\hat{S}_z, \hat{S}_x\right] = i\hbar\hat{S}_y$

附录

- 定义自旋角动量的升降算符
- $\hat{S}_+ = \hat{S}_x + i\hat{S}_y$
- $\hat{S}_- = \hat{S}_x - i\hat{S}_y$
- 升降算符有如下性质:
- $\hat{S}_+^* = \hat{S}_-$ $\hat{S}_-^* = \hat{S}_+$
- $\hat{S}_+\alpha = 0$ $\hat{S}_+\beta = \hbar\alpha$
- $\hat{S}_-\alpha = \hbar\beta$ $\hat{S}_-\beta = 0$
- $\left[\hat{S}_z, \hat{S}_+\right] = \hbar\hat{S}_+$ $\left[\hat{S}_z, \hat{S}_-\right] = -\hbar\hat{S}_-$
- $\left[\hat{S}_+, \hat{S}_-\right] = 2\hbar\hat{S}_z$
- $\hat{S}_+\hat{S}_- = \hat{S}^2 - \hat{S}_z^2 + \hbar\hat{S}_z$

附录

- 证明$\hat{S}_+\hat{S}_- = \hat{S}^2 - \hat{S}_z^2 + \hbar\hat{S}_z$

$$
\begin{aligned}
&\hat{S}_+\hat{S}_- \\
&= \left(\hat{S}_x + i\hat{S}_y\right)\left(\hat{S}_x - i\hat{S}_y\right) \\
&= \hat{S}_x^2 - i^2\hat{S}_y^2 + i\left(\hat{S}_y\hat{S}_x - \hat{S}_x\hat{S}_y\right) \\
&= \hat{S}_x^2 + \hat{S}_y^2 + i\left[\hat{S}_y, \hat{S}_x\right] \\
&= \hat{S}^2 - \hat{S}_z^2 - i^2\hbar\hat{S}_z \\
&= \hat{S}^2 - \hat{S}_z^2 + \hbar\hat{S}_z
\end{aligned}
$$

附录

- 证明$\left[\hat{S}_z,\hat{S}_+\right]=\hbar\hat{S}_+\qquad\left[\hat{S}_z,\hat{S}_-\right]=-\hbar\hat{S}_-$

$$
\begin{aligned}
&\left[\hat{S}_z,\hat{S}_+\right]\\
&=\hat{S}_z\hat{S}_+-\hat{S}_+\hat{S}_z\\
&=\hat{S}_z\left(\hat{S}_x+i\hat{S}_y\right)-\left(\hat{S}_x+i\hat{S}_y\right)\hat{S}_z\\
&=\hat{S}_z\hat{S}_x-\hat{S}_x\hat{S}_z+i\left(\hat{S}_z\hat{S}_y-\hat{S}_y\hat{S}_z\right)\\
&=\left[\hat{S}_z,\hat{S}_x\right]+i\left[\hat{S}_z,\hat{S}_y\right]\\
&=i\hbar\hat{S}_y-i^2\hbar\hat{S}_x\\
&=\hbar\left(\hat{S}_x+i\hat{S}_y\right)\\
&=\hbar\hat{S}_+
\end{aligned}
$$

同理可得，$\left[\hat{S}_z,\hat{S}_-\right]=-\hbar\hat{S}_-$

附录

- 证明$[\hat{S}_+, \hat{S}_-] = 2\hbar\hat{S}_z$

$$
\begin{aligned}
&[\hat{S}_+, \hat{S}_-] \\
&= \hat{S}_+\hat{S}_- - \hat{S}_-\hat{S}_+ \\
&= (\hat{S}_x + i\hat{S}_y)(\hat{S}_x - i\hat{S}_y) - (\hat{S}_x - i\hat{S}_y)(\hat{S}_x + i\hat{S}_y) \\
&= \hat{S}_x^2 - i^2\hat{S}_y^2 + i(\hat{S}_y\hat{S}_x - \hat{S}_x\hat{S}_y) \\
&\qquad - [\hat{S}_x^2 - i^2\hat{S}_y^2 + i(\hat{S}_x\hat{S}_y - \hat{S}_y\hat{S}_x)] \\
&= 2i(\hat{S}_y\hat{S}_x - \hat{S}_x\hat{S}_y) \\
&= 2i[\hat{S}_y, \hat{S}_x] \\
&= -2i^2\hbar\hat{S}_z \\
&= 2\hbar\hat{S}_z
\end{aligned}
$$

附录

- 证明$\hat{S}_+\beta=\hbar\alpha$

$\hat{S}_z\hat{S}_+\beta$

$=[\hat{S}_z,\hat{S}_+]\beta+\hat{S}_+\hat{S}_z\beta$

$=\hbar\hat{S}_+\beta-\frac{1}{2}\hbar\hat{S}_+\beta$

$=\frac{1}{2}\hbar\hat{S}_+\beta$

令$\psi=\hat{S}_+\beta$，

则有$\hat{S}_z\psi=\frac{1}{2}\hbar\psi$

则$\psi=\lambda\alpha$，即$\hat{S}_+\beta=\lambda\alpha$

$\langle\beta|\hat{S}_+^*\hat{S}_+|\beta\rangle=\lambda^2\langle\alpha|\alpha\rangle$

$\langle\beta|\hat{S}_-\hat{S}_+|\beta\rangle=\lambda^2$

$\langle\beta|\hat{S}^2-\hat{S}_z^2-\hbar\hat{S}_z|\beta\rangle=\lambda^2$

$\left(\frac{3}{4}\hbar^2-\frac{1}{4}\hbar^2+\frac{1}{2}\hbar^2\right)\langle\beta|\beta\rangle=\lambda^2$

$\hbar^2=\lambda^2$

取$\lambda=\hbar$，则

$\hat{S}_+\beta=\hbar\alpha$

附录

对以下4个波函数，可利用升降算符求得总自旋量子数

$$\Psi_1 = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)]\alpha(1)\alpha(2)$$

$$\Psi_2 = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)]\beta(1)\beta(2)$$

$$\Psi_3 = \frac{1}{2}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$\Psi_4 = \frac{1}{2}[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

设 $\phi_1 = \alpha(1)\alpha(2)$

$\phi_2 = \beta(1)\beta(2)$

$\phi_3 = \alpha(1)\beta(2) + \alpha(2)\beta(1)$

$\phi_4 = \alpha(1)\beta(2) - \alpha(2)\beta(1)$

附录

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$$
$$= \left(\hat{S}_{x1} + \hat{S}_{x2}\right)^2 + \left(\hat{S}_{y1} + \hat{S}_{y2}\right)^2 + \left(\hat{S}_{z1} + \hat{S}_{z2}\right)^2$$
$$= \left(\hat{S}_{x1}^2 + \hat{S}_{y1}^2 + \hat{S}_{x2}^2 + \hat{S}_{y2}^2\right) + \left(\hat{S}_{x1}\hat{S}_{x2} + \hat{S}_{x2}\hat{S}_{x1} + \right.$$

附录

$$\hat{S}^2 = \frac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-1} + \hat{S}_{-1}\hat{S}_{+1} + \hat{S}_{+2}\hat{S}_{-2} + \hat{S}_{-2}\hat{S}_{+2}\right)$$
$$+\frac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-2} + \hat{S}_{-1}\hat{S}_{+2} + \hat{S}_{-2}\hat{S}_{+1} + \hat{S}_{+2}\hat{S}_{-1}\right)$$
$$+\left(\hat{S}_{z1}^2 + \hat{S}_{z2}^2 + \hat{S}_{z1}\hat{S}_{z2} + \hat{S}_{z2}\hat{S}_{z1}\right)$$

$$\hat{S}^2\phi_1 = \hat{S}^2\alpha(1)\alpha(2)$$
$$= \frac{1}{2}\hbar^2[\alpha(1)\alpha(2) + 0 + \alpha(1)\alpha(2) + 0]$$
$$+\frac{1}{2}\hbar^2[0 + 0 + 0 + 0]$$
$$+\hbar^2(\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4})\alpha(1)\alpha(2)$$
$$= 2\hbar^2\alpha(1)\alpha(2)$$

故$S = 1$

附录

$$\hat{S}^2 = \frac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-1} + \hat{S}_{-1}\hat{S}_{+1} + \hat{S}_{+2}\hat{S}_{-2} + \hat{S}_{-2}\hat{S}_{+2}\right) + \frac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-2} + \hat{S}_{-1}\hat{S}_{+2} + \hat{S}_{-2}\hat{S}_{+1} + \hat{S}_{+2}\hat{S}_{-1}\right) + \left(\hat{S}_{z1}^2 + \hat{S}_{z2}^2 + \hat{S}_{z1}\hat{S}_{z2} + \hat{S}_{z2}\hat{S}_{z1}\right)$$

$$\begin{aligned}\hat{S}^2\phi_2 &= \hat{S}^2\beta(1)\beta(2) \\ &= \frac{1}{2}\hbar^2[0 + \beta(1)\beta(2) + 0 + \beta(1)\beta(2)] \\ &\quad + \frac{1}{2}\hbar^2[0 + 0 + 0 + 0] \\ &\quad + \hbar^2(\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4})\beta(1)\beta(2) \\ &= 2\hbar^2\beta(1)\beta(2)\end{aligned}$$

故$S = 1$

附录

$$\hat{S}^2 = \frac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-1} + \hat{S}_{-1}\hat{S}_{+1} + \hat{S}_{+2}\hat{S}_{-2} + \hat{S}_{-2}\hat{S}_{+2}\right)$$
$$+ \frac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-2} + \hat{S}_{-1}\hat{S}_{+2} + \hat{S}_{-2}\hat{S}_{+1} + \hat{S}_{+2}\hat{S}_{-1}\right)$$
$$+\left(\hat{S}_{z1}^2 + \hat{S}_{z2}^2 + \hat{S}_{z1}\hat{S}_{z2} + \hat{S}_{z2}\hat{S}_{z1}\right)$$

$$\hat{S}^2\phi_3 = \hat{S}^2[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$
$$= \frac{1}{2}\hbar^2[\alpha(1)\beta(2) + 0 + 0 + \alpha(2)\beta(1)$$
$$+0 + \alpha(2)\beta(1) + \alpha(1)\beta(2) + 0]$$
$$+ \frac{1}{2}\hbar^2[0 + \alpha(1)\beta(2) + \alpha(2)\beta(1) + 0$$
$$0 + \alpha(1)\beta(2) + \alpha(2)\beta(1) + 0]$$
$$+\hbar^2(\frac{1}{4} + \frac{1}{4} - \frac{1}{4} - \frac{1}{4})[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$
$$= 2\hbar^2[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

故$S = 1$

附录

$$
\begin{aligned}
\hat{S}^2 = &\frac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-1} + \hat{S}_{-1}\hat{S}_{+1} + \hat{S}_{+2}\hat{S}_{-2} + \hat{S}_{-2}\hat{S}_{+2}\right)\\
&+\frac{1}{2}\left(\hat{S}_{+1}\hat{S}_{-2} + \hat{S}_{-1}\hat{S}_{+2} + \hat{S}_{-2}\hat{S}_{+1} + \hat{S}_{+2}\hat{S}_{-1}\right)\\
&+\left(\hat{S}_{z1}^2 + \hat{S}_{z2}^2 + \hat{S}_{z1}\hat{S}_{z2} + \hat{S}_{z2}\hat{S}_{z1}\right)
\end{aligned}
$$

$$
\begin{aligned}
\hat{S}^2\phi_4 &= \hat{S}^2[\alpha(1)\beta(2) - \alpha(2)\beta(1)]\\
&= \frac{1}{2}\hbar^2[\alpha(1)\beta(2) - 0 + 0 - \alpha(2)\beta(1)\\
&\quad +0 - \alpha(2)\beta(1) + \alpha(1)\beta(2) - 0]\\
&\quad + \frac{1}{2}\hbar^2[0 - \alpha(1)\beta(2) + \alpha(2)\beta(1) - 0\\
&\quad +0 - \alpha(1)\beta(2) + \alpha(2)\beta(1) - 0]\\
&\quad +\hbar^2(\frac{1}{4} + \frac{1}{4} - \frac{1}{4} - \frac{1}{4})[\alpha(1)\beta(2) - \alpha(2)\beta(1)]\\
&= 0
\end{aligned}
$$

故$S = 0$