Part III Symmetry and Bonding

Chapter 3 Direct Products

Prof. Dr. Xin Lu（吕鑫）
Email: xinlu@xmu.edu.cn
http://pcossgroup.xmu.edu.cn/old/users/xlu/group/courses/theochem/

3. Direct products

- In this chapter we will learn how to find ***the symmetry of a product of two or more functions***.

  This is extraordinarily important!

  Recall those integrals we used before: $S_{ij} = \int \psi_i^* \psi_j d\tau$ $\beta = \int s_a \hat{H} s_b d\tau$

3.1 Introduction

- From the C_{2v} character table, we know that ***the function x transforms like B_1*** whereas ***the function y transforms like B_2***. *Then* ***how does the function xy transform?***

- This is already given in the table.

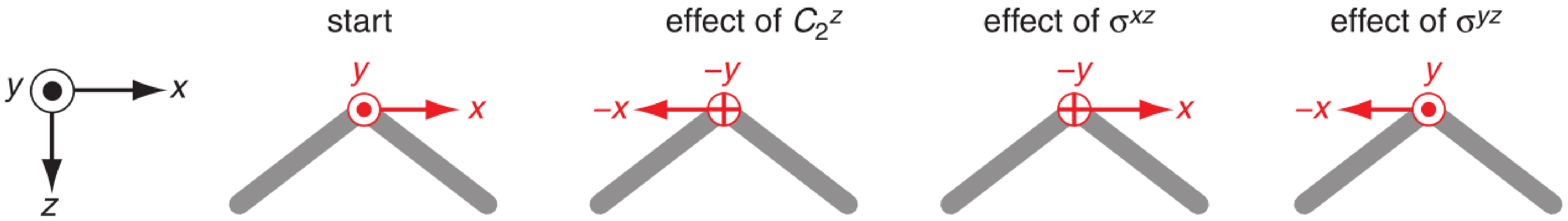
  The function xy transforms like A_2.

- How can we actually work this out?

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

3.1 Direct products introduction

- Use the function ***xy*** as a basis to form the corresponding representation of C_{2v}, which will just be ***a set of numbers***, i.e., these numbers are the ***characters***.



x	$Ex = (+1)x,$	$C_2^z x = (-1)x,$	$\sigma^{xz} x = (+1)x\ ,$	$\sigma^{yz} x = (-1)x\ ,$	(1,-1,1,-1) B_1
y	$Ey = (+1)y;$	$C_2^z y = (-1)y;$	$\sigma^{xz} y = (-1)y,$	$\sigma^{yz} y = (+1)y,$	(1,-1,-1,1) B_2
xy	$E(xy) = (+1)xy;$	$C_2^z xy = (+1)xy;$	$\sigma^{xz} xy = (-1)xy,$	$\sigma^{yz} xy = (-1)xy,$	(1,1,-1,-1) A_2

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

➢ ***xy*** transforms like A_2.

- The characters for ***xy*** are simply found by multiplying together the characters for the IR B_1, which is how ***x transforms***, and for the IR B_2, which is how ***y transforms***, operation by operation:

$$\underbrace{(1,-1,1,-1)}_{B_1\ (x)}\otimes\underbrace{(1,-1,-1,1)}_{B_2\ (y)}=(1\times1,-1\times-1,1\times-1,-1\times1)\equiv\underbrace{(1,1,-1,-1)}_{B_1\otimes B_2=A_2}$$

This kind of multiplication is called the ***direct product***: $B_1 \otimes B_2 = A_2$.

- To take another example, if we wanted to know how ***xz*** transforms:

$$\underbrace{(1,-1,1,-1)}_{B_1\ (x)}\otimes\underbrace{(1,1,1,1)}_{A_1\ (z)}=(1\times1,-1\times1,1\times1,-1\times1)\equiv\underbrace{(1,-1,1,-1)}_{B_1\otimes A_1=B_1}$$

Thus ***xz*** transforms like B_1.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

3.2 Direct product of one-dimensional irreducible representations

◆One-dimensional ***IR***s are those with character ***1*** under ***the operation E***, and always denoted by ***the labels A and B***.

全对称不可约表示

◆In any group there is always the ***totally symmetric IR*** with all of the characters being ***+1***.

◆For the *i*th one-dimensional ***IR***, $\Gamma^{(i)}$, of a group, the following properties apply:

1) The direct product of this ***IR*** with the ***totally symmetric IR***, $\Gamma^{tot.\ sym.}$, gives this ***IR***,

$$\Gamma^{(i)} \otimes \Gamma^{tot.\ sym.} = \Gamma^{(i)}$$

2) The direct product of a ***one-dimensional IR*** with itself gives the ***totally symmetric IR***

$$\Gamma^{(i)} \otimes \Gamma^{(i)} = \Gamma^{tot.\ sym.}$$

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

3.3 Direct product of two-dimensional irreducible representations

- Two-dimensional ***IR***s have character **2** under ***the identity operation***, and are always denoted by ***a label E***. (e.g., ***E*** IR in C_{3v})

C_{3v}	E	$2C_3^z$	$3\sigma_v$			
A_1	1	1	1	z		$x^2+y^2; z^2$
A_2	1	1	−1		R_z	
E	2	−1	0	(x, y)	(R_x, R_y)	$(xz, yz); (x^2-y^2, 2xy)$
$E \otimes E$	4	1	0	$= E \oplus A_1 \oplus A_2$		

- ***Property 1*** from the previous section still applies. For example, if we take the direct product $A_1 \otimes E$ we obtain ***E***.

$$\underbrace{(1,1,1)}_{A_1} \otimes \underbrace{(2,-1,0)}_{E} = (1\times 2, 1\times -1, 1\times 0) \equiv \underbrace{(2,-1,0)}_{E} \qquad \underbrace{(2,-1,0)}_{E} \otimes \underbrace{(2,-1,0)}_{E)} = (2\times 2, -1\times -1, 0\times 0) \equiv (4,1,0)$$

- ***Property 2*** does not apply. If we compute $E \otimes E$, we find $E \otimes E = E \oplus A_1 \oplus A_2$

- ***Modified version of property 2***: The direct product of an IR with itself ***contains*** the ***totally symmetric IR***. This trend holds for higher-dimensional ***IR***s.

3.4 Further points

- How does ***xyz*** transforms in the group C_{2v}? Consider the triple direct product:

$$\underbrace{B_1}_{x} \otimes \underbrace{B_2}_{y} \otimes \underbrace{A_1}_{z} = \underbrace{A_2}_{B_1 \otimes B_2} \otimes \underbrace{A_1}_{z} = A_2.$$

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

Thus ***xyz*** transforms as A_2.

- The direct product is commutative and distributive.

i.e. $B_1 \otimes B_2 = B_2 \otimes B_1$ and $(B_1 \otimes B_2) \otimes A_1 = B_1 \otimes (B_2 \otimes A_1)$.

- ***Simple numbers*** (scalars) transform as the ***totally symmetric IR***, as a number is ***unaffected*** by any symmetry operation.

Ex.13

3.5 Summary

- If *two functions* transform as the ***IR***s $\Gamma^{(i)}$ and $\Gamma^{(j)}$, respectively, then *their product* transforms as the *direct product* of the two ***IR***s $\Gamma^{(i)} \otimes \Gamma^{(j)}$.
- The *direct product* is found by *multiplying the characters* of the two ***IR***s for each symmetry operation: $(a, b, c, \ldots) \otimes (p, q, r, \ldots) = (a \times p, b \times q, c \times r, \ldots)$
- The ***totally symmetric IR***, $\Gamma^{tot.\ sym.}$, has character **+1** for all operations.
- For any ***IR*** $\Gamma^{(i)}$: $\Gamma^{(i)} \otimes \Gamma^{tot.\ sym.} = \Gamma^{(i)}$.
- For any one-dimensional ***IR***: $\Gamma^{(i)} \otimes \Gamma^{(i)} = \Gamma^{tot.\ sym.}$
- For any higher-dimensional ***IR*** the result of the product $\Gamma^{(i)} \otimes \Gamma^{(i)}$ contains $\Gamma^{tot.\ sym.}$.
- *Scalars* (*numbers*) transform as the ***totally symmetric IR***.