3.9: Direct Products

The intensity of a transition in the spectrum of a molecule is proportional to the magnitude squared of the transition moment matrix element.

$$\text{Intensity } \propto \left|\int (\psi')^* \vec{\mu}\, (\psi")\, d\tau\right|^2$$

By knowing the symmetry of each part of the integrand, the symmetry of the product can be determined as the **direct product** of the symmetries of each part $(\psi')^*$, $(\psi")$ and μ. This is helpful, since the integrand must not be antisymmetric with respect to any symmetry elements or the integral will vanish by symmetry. Before exploring that concept, let's look at the concept of direct products.

This is a concept many people have seen, in that the integral of an odd function over a symmetric interval, is zero. Recall what it means to be an "odd function" or an "even function.

Symmetry	**definition**	**Integrals**
Even	$f(-x) = f(x)$	$\int_{-a}^{a} f(x)dx = 2\int_0^a f(x)dx$
Odd	$f(-x) = -f(x)$	$\int_{-a}^{a} f(x)dx = 0$

Consider the function $f(x) = \left(x^3 - 3x\right) e^{-x^2}$. A graph of this function looks as follows:

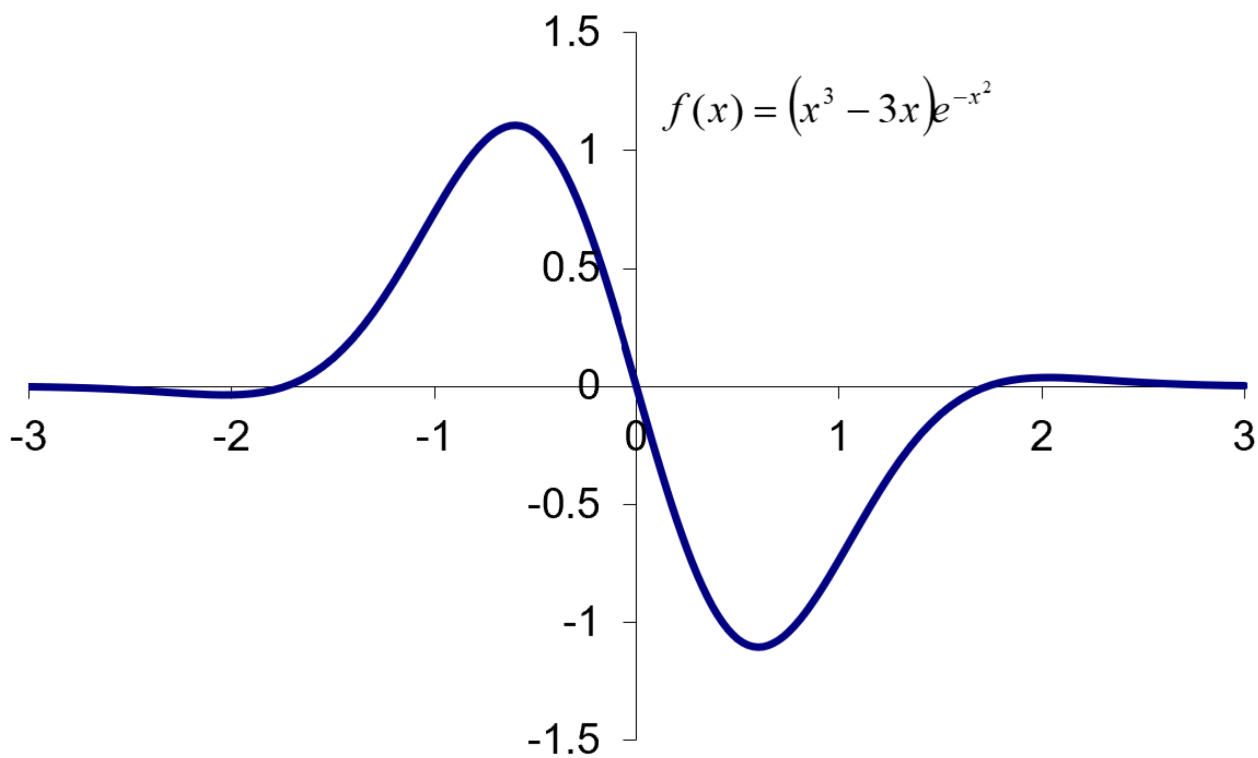

Figure 3.9.1

One notes that the area under the curve on the side of the function for which $x > 0$ has exactly the same magnitude but opposite sign of the area under the other side of the graph. Mathematically,

$$\begin{aligned} \int_{-a}^{a} f(x)dx &= \int_{-a}^{0} f(x)dx + \int_0^a f(x)dx \\ &= -\int_0^a f(x)dx + \int_0^a f(x)dx = 0 \end{aligned}$$

It is also interesting to note that the function *f(x)* can be expressed as the product of two functions, one of which is an odd function ($x^3 - 3x$) and the other which is an even function (e^{-x^2}). The result is an odd function. By determining the symmetry of the function as a product of the eigenvalues of the functions with respect to the inversion operator, as discussed below, one can derive a similar result.

The even/odd symmetry is an example of inversion symmetry. Recall that the inversion operator (in one dimension) affects a change of sign on x.

$$\hat{i}\, f(x) = f(-x)$$

“Even” and “odd” functions are eigenfunctions of this operator, and have eigenvalues of either +1 or –1. For the function used in the previous example,

$$f(x) = g(x)h(x)$$

where

$$g(x) = x^3 - 3x \text{ and } h(x) = e^{-x^2}$$

Here, $g(x)$ is an odd function and $h(x)$ is an even function. The product is an odd function. This property is summarized for any $f(x) = g(x)h(x)$, in the following table.

g(x)	h(x)	f(x)	ig(x)=__g(x)	ih(x)=__h(x)	if(x)=__f(x)
even	even	even	1	1	1
even	odd	odd	1	-1	-1
odd	odd	even	-1	-1	1

Note that the eigenvalue (+1 or –1) is simply the character of the inversion operation for the irreducible representation by which the function transforms! In a similar manner, any function that can be expressed as a product of functions (like the integrand in the transition moment matrix element) can be determined as the direct product of the irreducible representations by which each part of the product transforms.

Consider the point group C_{2v} as an example. Recall the character table for this point group.

C_{2v}	E	C_2	σ_v	σ_v ’			
A_1	1	1	1	1	z		$x^2 - y^2$, z^2
B_2	1	-1	-1	1	y	R_x	yz
B_1	1	-1	1	-1	x	R_y	xz
A_2	1	1	-1	-1		R_z	xy

The direct product of irreducible representations can by the definition

$$\chi_{prod}(R) = \chi_i(R) \otimes \chi_j(R)$$

So for the direct product of B_1 and B_2, the following table can be used.

C_{2v}	E	C_2	σ_v	σ_v ’
B_1	1	-1	1	-1
B_2	1	-1	-1	1
$B_1 \otimes B_2$	1	1	-1	-1

The product is actually the irreducible representation given by A_2 ! As it turns out, the direct product will always yield a set of characters that is either an irreducible representation of the group, or can be expressed as a sum of irreducible representations. This suggests that a multiplication table can be constructed. An example (for the C_{2v} point group) is given below.

Studying this table reveals some useful generalizations. Two things in particular jump from the page. These are summarized in the following tables.

	A	B
A	A	B
B	B	A

	1	2
1	1	2
2	2	1

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

This pattern might seem obvious to some. It stems from the idea that

*symmetric*symmetric = symmetric*

*symmetric*antisymmetric = antisymmetric*

*antisymmetric*antisymmetric = symmetric*

Noting that A indicates that an irreducible representation is *symmetric* with respect to the C_2 operation and B indicates that an irreducible representation is *antisymmetric* . . and that the subscript 1 indicates that an irreducible representation is *symmetric* with respect to the σ_v operation, and that a subscript 2 indicates that an irreducible representation is *antisymmetric* . . the rest seems to follow! Some point groups have irreducible representations use subscripts g/u or primes and double primes. The g/u subscript indicates symmetry with respect to the inversion (i) operator, and the prime/double prime indicates symmetry with respect to a σ plane (generally the plane of the molecule for planar molecules).

This method works well for singly degenerate representations. But what does one do for products involving doubly degenerate representations? As an example, consider the C_{3v} point group.

C_{3v}	E	2 C_3	$3\sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	(x, y)	(R_x, R_y)

Consider the direct product of A_2 and E.

C_{3v}	E	2 C_3	3 σ_v
A_2	1	1	-1
E	2	-1	0
$A_2 \otimes E$	2	-1	0

This product is clearly just the E representation. Now one other example – Consider the product $E \otimes E$.

C_{3v}	E	2 C_3	$3\sigma_v$
E	2	-1	0
E	2	-1	0
$E \otimes E$	4	1	0

To find the irreducible representations that comprise this reducible representation, we proceed in the same manner as determining the number of vibrational modes belonging to each symmetry.

$$\begin{aligned} N_{A_1} &= \frac{1}{6}[(1)(4)+2(1)(1)+3(1)(0)] = 1 \\ N_{A_2} &= \frac{1}{6}[(1)(4)+2(1)(1)+3(-1)(0)] = 1 \\ N_E &= \frac{1}{6}[(2)(4)+2(-1)(1)+3(0)(0)] = 1 \end{aligned}$$

This allows us to build a table of direct products. Notice that the direct product always has the total dimensionality that is given by the product of the dimensions.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	$A_1 + A_2 + E$

The concepts developed in this chapter will be used extensively in the discussions of vibrational, rotational and electronic degrees of freedom in atoms and molecules.