

# A UNIVERSAL TRUTH: (from Lecture 19)

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The Expectation Value of ANY operator  $A$  is given by:

**the trace of the product of the Density Matrix  
and the operator Matrix**

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## A MORE UNIVERSAL TRUTH:

**ANY MATRIX ELEMENT** (not just expectation value) of ANY operator  $A$  is given by:

**the trace of the product of the Transition Density Matrix and the operator Matrix**

"Transition Density" =  $\psi_2 \psi_1^*$  = product of 2 different functions

We can see that in a sense,  $A_{12}$  is the overlap integral of the operator and the transition density.

$$A_{12} = \int \Psi_1^* \hat{A} \Psi_2 d\tau = \int \hat{A} \Psi_2 (\Psi_1^*) d\tau$$

where the parentheses mean  $\hat{A}$  does not operate on  $\Psi_1^*$

This is better seen in bra-ket notation:

$$\begin{aligned}
A_{12} &= \langle \Psi_1^* | \hat{A} | \Psi_2 \rangle \\
&= \langle \Psi_1^* | \sum_m | m \rangle \langle m | \hat{A} | \sum_n \langle n | \Psi_2 \rangle \\
&= \sum_m \sum_n \langle \Psi_1^* | m \rangle \langle m | \hat{A} | n \rangle \langle n | \Psi_2 \rangle \\
&= \sum_m \sum_n c_{\Psi_1 m}^* A_{mn} c_{n \Psi_2} = \sum_m \sum_n c_{n \Psi_1} c_{\Psi_2 m}^* A_{mn} \\
&= \sum_m \sum_n P_{nm}^{1,2} A_{mn} = \sum_n \sum_m P_{nm}^{1,2} A_{mn} = \sum_n (P^{1,2} A)_{nn}
\end{aligned}$$

$= \text{trace}(P^{1,2} A)$  = sum of diagonal elements of the product of the Transition Density matrix and matrix of operator  $A$

Careful inspection, however, shows that the words used to state this operation **disguise** the underlying simplicity. The operation is indeed like tracing one matrix on the other. Taking the trace of the matrix product is distracting information.

For a **symmetric** real matrix:

$$A_{12} = \sum_m \sum_n P_{nm}^{12} A_{mn} = \sum_{mn} P_{nm}^{12} A_{mn} = P_{mn}^{12} A_{mn}$$

This is simply the sum of the products of all the corresponding matrix elements, taken in any order. This is the **SCALAR PRODUCT** of the two matrices, i.e., completely analogous to the overlap integral of the matrices.

0 1 0 <b>1</b> 0	7 0 1 <b>4</b> 5
1 0 1 0 1	0 6 0 9 0
0 1 0 1 0	1 0 0 0 5
1 0 1 0 1	0 9 0 7 0
0 <b>1</b> 0 1 0	1 <b>8</b> 0 0 0

The pattern in the left matrix (transition density) is that all elements whose sum of row-col indices is **EVEN = 0** and if **ODD = 1**, so you can quickly see that the trace of the product of these two matrices is **12**.

This formalism is also hidden in Levine's off diagonal matrix element of the Fock matrix.

# CIS-type Excited states with DFT

Use the td keyword meaning time dependent DFT,  
Search for excited state in the .out file.

Example:

```
%chk=straw-cis.chk  
# b3lyp/3-21g pop=reg td(nstates=3)
```

Strawberry excited singlet states

```
-1 1  
C      0.288553 -0.419651  1.468809  
N     -0.254081 -0.324906  0.287482  
N      0.585932  0.922271  1.993822  
....
```

Feels just like using CIS with wavefunction methods  
Excited states obtained by finding resonant  
frequencies by applying an oscillating electric field.

# Symmetry and Group Theory

## Goal of this section

1. To relate symmetry operations and group theory language to general theorems of quantum mechanics and matrix techniques used in this course.
2. In particular, clarify the concept of representations, irreducible representations, bases of representations, "character", and how to read a character table.

# Symmetry operators

## (1) Moving the atoms (coordinates change)

- a **rotation** about an axis through the center of the molecule,
- or • a **reflection** through a plane passing through the center,
- or • a **combination** of rotation and reflection

**RESULT:** atom ends up in the same position or a position vacated by an equivalent atom;

## OR, (2) Rotate the coordinate system (atoms stay put)

a transformation of the coordinate system via rotation and/or reflection such that an atom's new coordinates are the same as before or the same as some equivalent atoms were before. -note : equivalent means same surroundings as well as same atomic number.

**This is what quantum mechanical operators do.**

# Two Important Theorems relating to Symmetry

## Levine: Theorem 5 (p. 168)

If two operators **commute**, it is possible to select a common, complete set of eigenfunctions for them.

**Levine: Theorem 6 (p. 169)** If two wavefunctions  $\psi_1$  and  $\psi_2$  are eigenfunctions of an operator that commutes with the Hamiltonian and have different eigenvalues, then  $\langle \psi_1 | H | \psi_2 \rangle = 0$ .

**Fact: All symmetry operations commute with the Hamiltonian**

## Paraphrased to emphasize symmetry:

If two wavefunctions  $\psi_1$  and  $\psi_2$  "have different symmetry", i.e., belong to different irreducible representations (have different eigenvalues of the sym. Op., they will not "interact" (i.e., the Hamiltonian matrix element,  $\langle \psi_1 | H | \psi_2 \rangle$ , between them **must vanish**)

The practical value of this is that a large Hamiltonian matrix need not be diagonalized. H matrix becomes "block diagonalized" into a series of smaller matrices whose dimension = the number of basis functions that have a particular symmetry (are representatives of a particular irreducible representation).

## Significance of Symmetry and Group Theory to Quantum Chemistry:

*Hamiltonian* is **invariant** under a symmetry operation.

Because  $H$  is unchanged by a symmetry operation (by definition), **symmetry operations always commute with  $H$** ,

This means that the energy eigenfunctions may be constructed so as to be simultaneously **eigenfunctions of the symmetry operations**.

Note the similarity to angular momentum operators,  $L$  and  $L_z$  (for spherical systems).

(These operators actually rotate the coordinate system.)

The **set** of “eigenvalues” (commonly called “characters”) of the **set** of symmetry operators for a molecule are used to **classify** wavefunctions, and products of wavefunctions and operators. (just as s, p, d, f, ... classify atomic orbitals as to eigenvalue of  $L^2$ .)

Great utility comes from one simple fact:

For a symmetric molecule, if  $\Psi_1$  and  $\Psi_2$  have different symmetry

classification, then 
$$\int_{-\infty}^{\infty} \Psi_1^* H \Psi_2 d\tau = 0$$

because **nodes** in the product  $\Psi_1^* \Psi_2$  ensure that the **negative parts of the integral cancel the positive parts**

Thus, knowing symmetry classifications of wavefunctions (which come from *character tables*), GREATLY simplifies linear variation calculations, and other calculations that depend on knowing matrix elements.

Trying to mix functions with different symmetry will not help lower the energy.

For example if  $\Psi_1$  and  $\Psi_2$  have “symmetry”  $A_{2u}$  and  $\Psi_3$  and  $\Psi_4$  have “symmetry”:  $B_{1g}$ , then the H matrix becomes block diagonalized, i.e., the 4x4 matrix become two completely separate 2x2 matrices, which you can do approximately in your head :).

$$\begin{array}{cccc}
 H_{11} & H_{12} & H_{13} & H_{14} \\
 H_{21} & H_{22} & H_{23} & H_{24} \\
 H_{31} & H_{32} & H_{33} & H_{34} \\
 H_{41} & H_{42} & H_{43} & H_{44}
 \end{array}
 \quad \longrightarrow \quad
 \begin{array}{cccc}
 H_{11} & H_{12} & 0 & 0 \\
 H_{21} & H_{22} & 0 & 0 \\
 0 & 0 & H_{33} & H_{34} \\
 0 & 0 & H_{43} & H_{44}
 \end{array}$$

## Symmetry classifications come from Group Theory

**Group:** The point group characterizing a given molecule is the set of all operations which are symmetry operations on the molecule. This set of symmetry operations conforms to the formal definition of a **group**. (Levine, Chap. 12)

Groups are named by symbols such as  $C_{3v}$  (ammonia),  $D_{2h}$  (formaldehyde),  $D_{6h}$  (benzene),  $Td$  (methane), etc.

Note: The definition of a group essentially means that one can construct a "***multiplication table***", which in this case means successive operation by any two of the symmetry operations is equivalent to operating with another member of the group.

In specifying a molecule's point group symmetry we say it has  $D_{2h}$  symmetry, for example.

## The next 6 pages are a more compact and technical statement of the connection between symmetry and quantum chemistry

### Why Study Symmetry and Group Theory ?

This can be summarized by two theorems:

- (I) The energy eigenfunctions (and also molecular orbitals) must be bases\* for the irreducible\* representations\* (I. R. 's) of its symmetry group.

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\* Hang on! These strange words will hopefully be clarified on the next page.

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- (II) (a) If two functions (could be atomic or molecular orbitals, or sums and/or products thereof,)  $\psi_1$  and  $\psi_2$ , "have different symmetry" (which means they are bases for different irreducible representations of the molecule's symmetry group) they will not "interact." That is,

$$\int \psi_1 H \psi_2 dt = 0 \quad \text{where H is the molecule's Hamiltonian operator.}$$

- (b) if  $\psi_1$  and  $\psi_2$  are energy eigenfunctions (or molecular orbitals) they must have different energies (except in rare cases of accidental degeneracy) if they have different symmetry.

If  $\psi_1$  and  $\psi_2$  are a basis set for the same I. R., they must have the same energy.

Thus, when seeking the eigenfunctions for a molecule having symmetry one need not bother mixing together functions with different symmetry and one can solve several small matrix problems (one for each type of symmetry) instead of one big matrix.

Actually, when dealing with matrix elements of operators other than energy it is also possible to predict when the integral will be zero using group theory. Examples are selection rules for absorption of light, dipole moments, optical rotation, etc.

With respect to theorem II(b) it is important to realize that this is why the Woodward-Hoffman rules work.

## Clarifications

### 1. What is a representation of a group?

Simply a set of numbers or matrices which can be substituted for the members of the group so as to have the same multiplication table (~~see p. 95 of text~~). The simplest representation of a group is where each member is represented by the number 1. On page 99 are shown 3 different representations of the  $C_{3v}$  group. Two are 1-dimensional and one is 2-dimensional, i. e., a set of 2 x 2 matrices.

### 2. What is meant by a basis for a representation?

A basis for an n-dimensional representation of a group is simply n different functions from which the representation (set of matrices) can be generated:

Let the basis be  $\varphi_1, \varphi_2, \varphi_3 \dots \varphi_n$ . The representative matrix for a given symmetry operation,  $\sigma_i$ , is generated by operating on each of the n functions.

$$\text{Thus, if } \sigma_i \varphi_1 = a_{11}^i \varphi_1 + a_{12}^i \varphi_2 + \dots + a_{1n}^i \varphi_n$$

$$\sigma_i \varphi_2 = a_{21}^i \varphi_1 + a_{22}^i \varphi_2 + \dots + a_{2n}^i \varphi_n$$

$$\vdots$$
$$\sigma_i \varphi_n = a_{n1}^i \varphi_1 + a_{n2}^i \varphi_2 + \dots + a_{nn}^i \varphi_n$$

the matrix representing  $\mathcal{O}_i$  is

$$R_i = \begin{pmatrix} a_{11}^i & a_{12}^i & \dots & a_{1n}^i \\ a_{21}^i & & & \\ a_{31}^i & & & \\ \vdots & & & \\ a_{n1}^i & a_{n2}^i & \dots & a_{nn}^i \end{pmatrix}$$

Notice that the only requirement is that each operation cause each basis function to go into a function which is a linear combination of the members of the basis set.

### 3. What is meant by irreducible?

Example:

If two functions are a basis for a 2-dimensional irreducible representation, this means there is no way to transform the 2 functions into two new ones which are each basis functions for a one-dimensional representation. *i.e.* are both diagonal.

Example:  $\mathcal{O}_i p_x = a_{11}^i p_x + a_{12}^i p_y$

and  $\mathcal{O}_i p_y = a_{21}^i p_x + a_{22}^i p_y$  for each operation  $\mathcal{O}_i$ .

The representation (i.e. the set of 2 x 2 matrices  $R_i$  is reducible if one can find new linear combinations:

$$p_1 = c_{11}p_x + c_{12}p_y$$

$$p_2 = c_{21}p_x + c_{22}p_y$$

such that

$$\mathcal{O}_i p_1 = p_1 \quad \text{or} \quad \mathcal{O}_i p_1 = -p_1$$

and  $\mathcal{O}_i p_2 = p_2$  or  $\mathcal{O}_i p_2 = -p_2$  for every  $\mathcal{O}_i$ .

In other words, if we cannot find linear combinations of  $p_x$  and  $p_y$  which simply go into + or - themselves for each operation of the group then  $p_x$  and  $p_y$  are a basis for a 2-dimensional irreducible representation of the group.

~~(See pages 96-97 in text).~~

#### 4. Character Tables

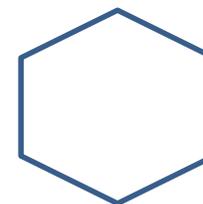
The various irreducible representations of a group are tabulated and labeled in character tables.

Character = the sum of the diagonal elements of the matrix that represents a particular operation. **i.e., the TRACE**

In a one-dimensional representation the characters are therefore the representation. For n-dimensional representations the character (trace) is tabulated since it is invariant to transformations of the basis set and it is all that is needed to characterize an irreducible representation.

Conventions for labeling:	one dimensional	A & B
	two dimensional	E
	three dimensional	T (or F)
	four dimensional	G
	etc.	

# Example: Character Table for the $D_{6h}$ point group, to which benzene belongs



$D_{6h}$	$E$	$2C_6$	$2C_3$	$C_2$	$3C'_2$	$3C''_2$	$i$	$2S_3$	$2S_6$	$\sigma_h$	$3\sigma_d$	$3\sigma_v$		
$A_g$	1	1	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1	$R_z$	
$B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
$B_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
$E_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$E_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$
$A_{1u}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	$z$	
$B_{1u}$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
$E_{1u}$	2	1	-1	-2	0	0	-2	-1	1	2	0	0	$(x, y)$	
$E_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

$A_{1g}$  is always **totally symmetric** (characters are all= 1)

**The symbols in the two right-hand columns have the following meanings:**

The position operators  $x, y, p_x$  and  $p_y$  orbitals have  $E_{1u}$  symmetry

The  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals have  $E_{2g}$  symmetry, etc.