Names for the various pure DFT models are given by combining the names for the exchange and correlation functionals. In some cases, standard synonyms used in the field are also available as keywords. In order to specify a pure functional, combine an exchange functional component keyword with the one for desired correlation functional. For example, the combination of the Becke exchange functional (B) and the LYP correlation functional is requested by the BLYP keyword. Similarly, SVWN requests the Slater exchange functional (S) and the VWN correlation functional, and is known in the literature by its synonym LSDA (Local Spin Density Approximation). LSDA is a synonym for SVWN. Some other software packages with DFT facilities use the equivalent of SVWN5 when "LSDA" is requested. Check the documentation carefully for all packages when making comparisons.

Exchange Functionals

The following exchange functionals are available in Gaussian 16. Unless otherwise indicated, these exchange functionals must be combined with a correlation functional in order to produce a usable method.

•S: The Slater exchange, $\rho^{4/3}$ with theoretical coefficient of 2/3, also referred to as Local Spin Density exchange [Hohenberg64, Kohn65, Slater74]. Keyword if used alone: HFS.

•XA: The XAlpha exchange, $\rho^{4/3}$ with the empirical coefficient of 0.7, usually employed as a standalone exchange functional, without a correlation functional [Hohenberg64, Kohn65, Slater74]. Keyword if used alone: XAlpha.

•B: Becke's 1988 functional, which includes the Slater exchange along with corrections involving the gradient of the density [Becke88b]. Keyword if used alone: HFB.

•PW91: The exchange component of Perdew and Wang's 1991 functional [Perdew91, Perdew92, Perdew93a, Perdew96, Burke98].

•mPW: The Perdew-Wang 1991 exchange functional as modified by Adamo and Barone [Adamo98].

•G96: The 1996 exchange functional of Gill [Gill96, Adamo98a].

•PBE: The 1996 functional of Perdew, Burke and Ernzerhof [Perdew96a, Perdew97].

•O: Handy's OPTX modification of Becke's exchange functional [Handy01, Hoe01].

•TPSS: The exchange functional of Tao, Perdew, Staroverov, and Scuseria [Tao03].

•RevTPSS: The revised TPSS exchange functional of Perdew et. al. [Perdew09, Perdew11].

•BRx: The 1989 exchange functional of Becke [Becke89a].

•PKZB: The exchange part of the Perdew, Kurth, Zupan and Blaha functional [Perdew99].

•wPBEh: The exchange part of screened Coulomb potential-based final of Heyd, Scuseria and Ernzerhof (also known as HSE) [Heyd03, Izmaylov06, Henderson09].

•PBEh: 1998 revision of PBE [Ernzerhof98].

Correlation Functionals

The following correlation functionals are available, listed by their corresponding keyword component, all of which must be combined with the keyword for the desired exchange functional:

•VWN: Vosko, Wilk, and Nusair 1980 correlation functional(III) fitting the RPA solution to the uniform electron gas, often referred to as Local Spin Density (LSD) correlation [Vosko80] (functional III in this article).

•VWN5: Functional V from reference [Vosko80] which fits the Ceperly-Alder solution to the uniform electron gas (this is the functional recommended in [Vosko80]).

•LYP: The correlation functional of Lee, Yang, and Parr, which includes both local and non-local terms [Lee88, Miehlich89].

•PL (Perdew Local): The local (non-gradient corrected) correlation functional of Perdew (1981) [Perdew81].

•P86 (Perdew 86): The gradient corrections of Perdew, along with his 1981 local correlation functional [Perdew86].

•PW91 (Perdew/Wang 91): Perdew and Wang's 1991 gradient-corrected correlation functional [Perdew91, Perdew92, Perdew93a, Perdew96, Burke98].

•B95 (Becke 95): Becke's τ-dependent gradient-corrected correlation functional (defined as part of his one parameter hybrid functional [Becke96]).

•PBE: The 1996 gradient-corrected correlation functional of Perdew, Burke and Ernzerhof [Perdew96a, Perdew97].

•TPSS: The τ-dependent gradient-corrected functional of Tao, Perdew, Staroverov, and Scuseria [Tao03].

•RevTPSS: The revised TPSS correlation functional of Perdew et. al. [Perdew09, Perdew11].

•KCIS: The Krieger-Chen-Iafrate-Savin correlation functional [Rey98, Krieger99, Krieger01, Toulouse02].

•BRC: Becke-Roussel correlation functional [Becke89a].

•PKZB: The correlation part of the Perdew, Kurth, Zupan and Blaha functional [Perdew99].

Correlation Functional Variations. The following correlation functionals combine local and non-local terms from different correlation functionals:

•VP86: VWN5 local and P86 non-local correlation functional.

•V5LYP: VWN5 local and LYP non-local correlation functional.

Standalone Pure Functionals

The following pure functionals are self-contained and are not combined with any other functional keyword components:

•VSXC: van Voorhis and Scuseria's τ-dependent gradient-corrected correlation functional [VanVoorhis98].

•HCTH/*: Handy's family of functionals including gradient-corrected correlation [Hamprecht98, Boese00, Boese01]. HCTH refers to HCTH/407, HCTH93 to HCTH/93, HCTH147 to HCTH/147, and HCTH407 to HCTH/407. Note that the related HCTH/120 functional is not implemented.

•tHCTH: The τ-dependent member of the HCTH family [Boese02]. See also tHCTHhyb below.

•B97D: Grimme's functional including dispersion [Grimme06]. B97D3 requests the same but with Grimme's D3BJ dispersion [Grimme11].

•M06L [Zhao06a], SOGGA11 [Peverati11], M11L [Peverati12], MN12L [Peverati12c] N12 [Peverati12b] and MN15L [Yu16a] request these pure functionals from the Truhlar group.

Symmetry and Group Theory

Goals 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 concepts of representations, *irreducible* representations, *bases* of representations, "character", and how to read a character table.

Character== SUM of Eigenvalues = _Trace_ of representative matrix (usually) = +1 or -1 =trace of a 1 dimensional matrix
With certain symmetries the character =the <u>Trace</u> of a matrix representing a symmetry operator that mixes degenerate wavefunctions

3. Orthogonality of sets of characters ; projection operators

Symmetry operators: operations that "appear" to do nothing

(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.

r17

Symmetry and Group Theory

Symmetry classifications come from Group Theory

Group Theory began in ~1830:
Mathematicians did this for **fun** –**not** because they thought
it could be useful.

The Grand Statement of Why We Learn about Molecular Symmetry and Group Theory:

The eigenfunctions of the Hamiltonian for a molecule with one or more *elements of symmetry*
are *bases (a basis set)* for the
irreducible representations
of the *point group* of the symmetry **operators** of the that molecule.

The underlined words are the same as for quantum operators, which have basis sets and representations, i.e., representatives

Two Important QM 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 ψ_1 and ψ_2 are eigenfunctions of
an operator that commutes with the Hamiltonian and have different eigenvalues,
then $<\psi_1|H|\psi_2> = 0$.

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

Paraphrased to emphasize symmetry:

**If two wavefunctions ψ_1 and ψ_2 "have different symmetry", ie., belong to
different irreducible representations (have a different set of eigenvalues for the
symmetry operators, they will not "interact" (i.e., the Hamiltonian matrix
element, $<\psi_1|H|\psi_2>$, between them must vanish)**

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

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

Block Diagonal

irreducible representation matrices remain Block Diagonal
are those basis function that are degenerate in energy

Point Group: applies to single molecules which contain a unique point that is invariant (does not move) for any of the symmetry operations: the center of mass)

Space Group: e.g., crystals. Translation of a unit cell is a symmetry operator

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)

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.

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

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

C$_4$ point group Multiplication Table

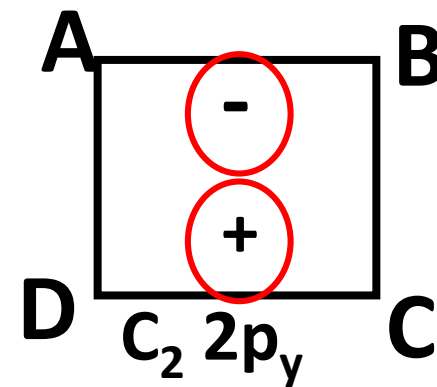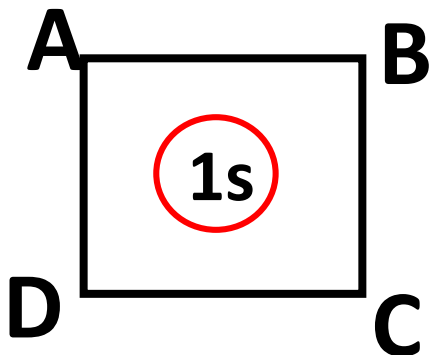|	I	C$_4^+$	C$_4^-$	C$_2$
I	I	C$_4^+$	C$_4^-$	C$_2$
C$_4^+$	C$_4^+$	C$_2$	I	C$_4^-$
C$_4^-$	C$_4^-$	I	C$_2$	C$_4^+$
C$_2$	C$_2$	C$_4^-$	C$_4^+$	I

A ___ B

D ___ C
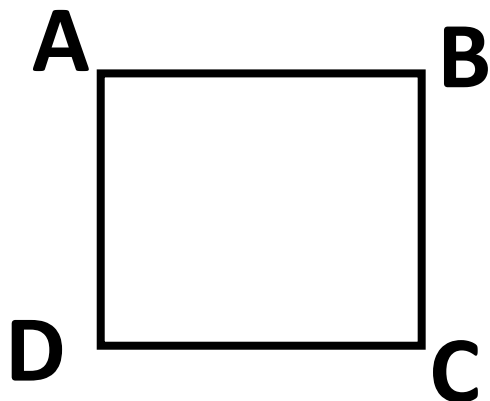
For this object, consider only rotations about the axis perp. to plane.
there are other symmetry operations, such as reflection in the plane, but we assume something is not symmetrical out of plane

You can see that all multiplications give a member of the group

Which of the functions are eigenfunctions of the operators?

A ___ B (1s) D ___ C

A ___ B (+ / -) D ___ C 2p$_y$

A ___ B (' +) D ___ C C$_4^+$ 2p$_y$

A ___ B (- / +) D ___ C C$_2$ 2p$_y$
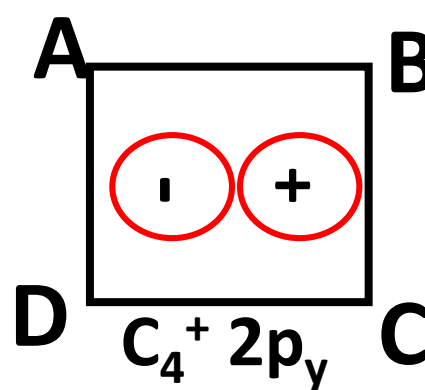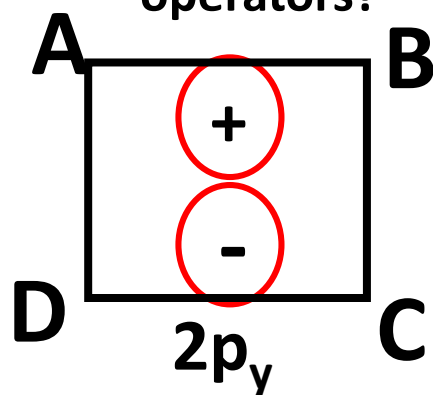
If A=B=C=D, would say object is in C4 point group "C4 symmetry"

C_4 Character (Eigenvalue) Table

	I	C_4^+	C_4^-	C_2	
A	1	1	1	1	z
B	1	-1	-1	1	
E					

e Chemical Portal www.webqc.org

Character table

	E	C_4	C_2	$(C_4)^3$	linear, rotations	quadratic
A	1	1	1	1	z, R_z	x^2+y^2, z^2
B	1	-1	1	-1		x^2-y^2, xy
E	1	i	-1	-i	$x+iy, R_x+iR_y$	(yz, xz)
	1	-i	-1	i	$x-iy, R_x-iR_y$	

1s
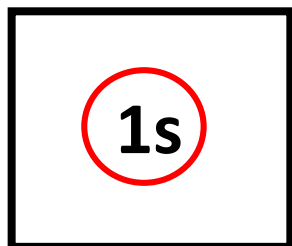
I and C_2
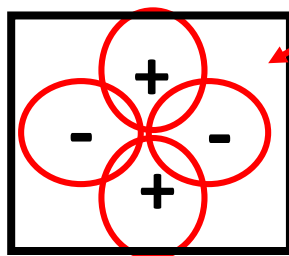
C_4^+ and C_4^-
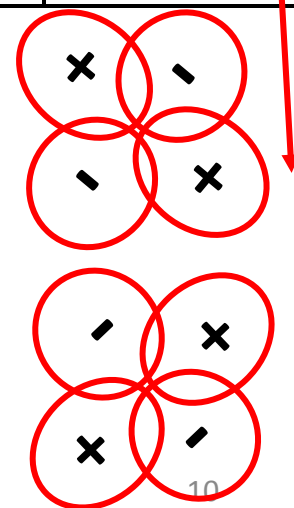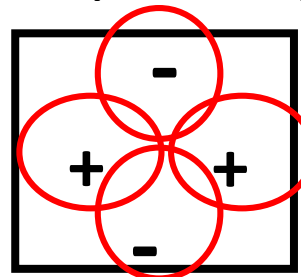
Group C$_3$ Multiplication Table

	I	C$_3^+$	C$_3^-$
I	I	C$_3^+$	C$_3^-$
C$_3^+$	C$_3^+$	C$_3^-$	I
C$_3^-$	C$_3^-$	I	C$_3^+$

1s
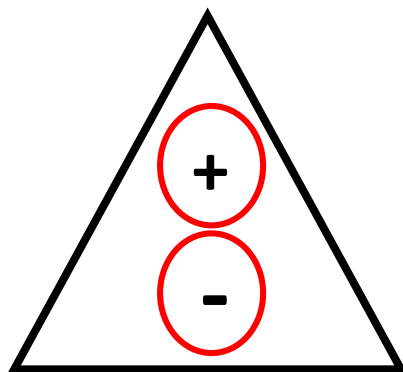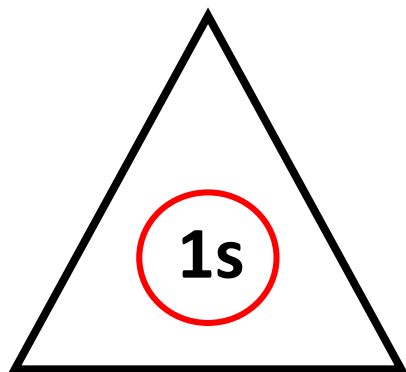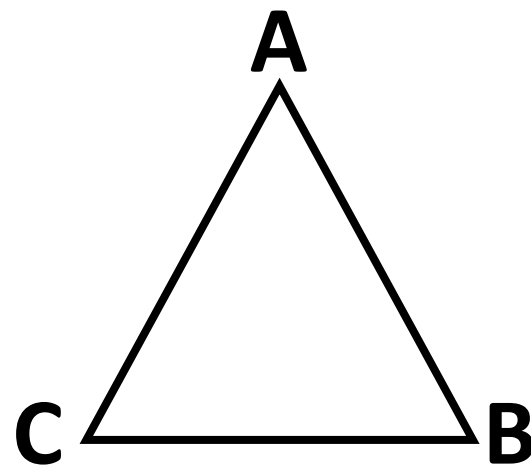
2p$_y$
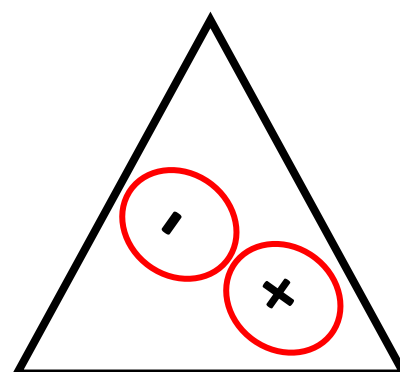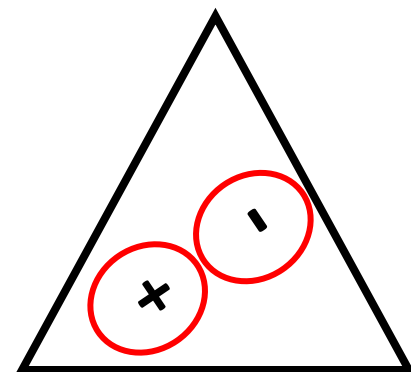
C$_3^+$ 2p$_y$

C$_3^-$ 2p$_{y_1}$

Group C₃ Character Table

	I	C_3^+	C_3^-		
A	1	1	1	z	z^2, x^2+y^2
E	2	-1	-1	x,y	x^2-y^2 xy

1s

p_x

p_y

$C_3^+ 2p_y$
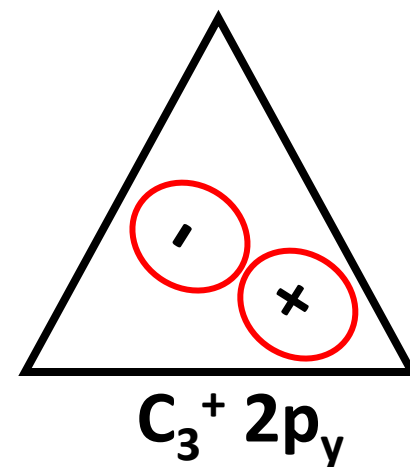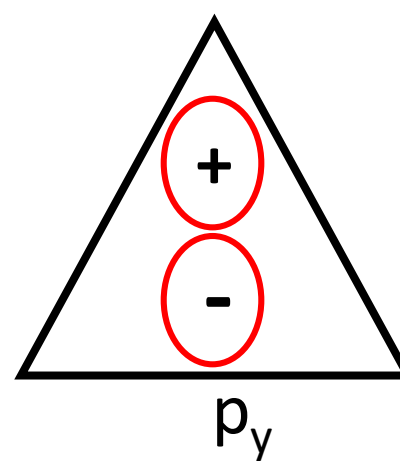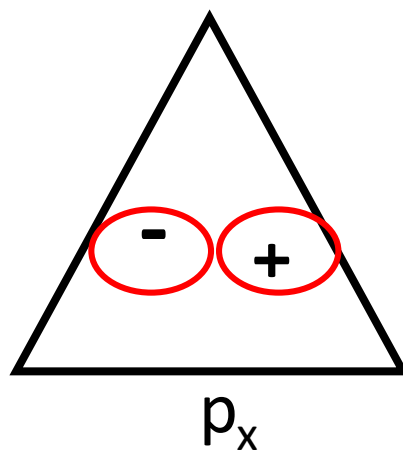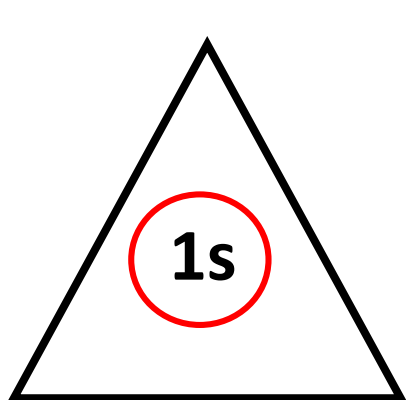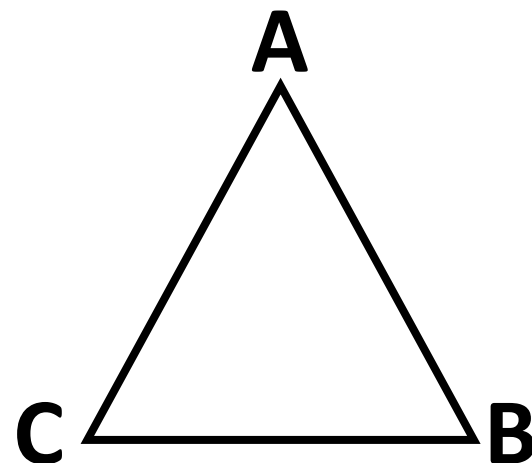
What is the energy difference for the 3 orientations if there a proton at each corner??? **NONE**

Creating representations of the member of the Group of symmetry operators

The representatives (representations) are matrices generated by applying the operators to basis functions

Consider the effect of applying the identity, *I,* to p_x and p_y

$$I \begin{pmatrix} p_x \\ p_y \end{pmatrix} = \begin{matrix} 1p_x + & 0p_y \\ 0p_x + & 1p_y \end{matrix} == \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix}$$

The character = the trace = 2

Consider the effect of applying C_3^+ (120^0 CW rotatation) to p_x and p_y

$$C_4^+ \begin{pmatrix} p_x \\ p_y \end{pmatrix} = \begin{matrix} -\dfrac{1}{2}p_x + & \dfrac{\sqrt{3}}{2}p_y \\ \dfrac{\sqrt{3}}{2}p_x + & -\dfrac{1}{2}p_y \end{matrix} = \begin{pmatrix} -\dfrac{1}{2} & \dfrac{\sqrt{3}}{2} \\ \dfrac{\sqrt{3}}{2} & -\dfrac{1}{2} \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix}$$

The character = the trace = -1

That is exactly what the character table says for x,y which is what px and py are. Thus, p_x and p_y belong to the E irreducible representation. (E always indicates dimension = 2

Group C_3 Character Table

	I	C_3^+	C_3^-		
A	1	1	1	z	z², x²+y²
E	2	-1	-1	x,y	x²-y², xy

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.

_____

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

_____

(II)   (a) If two functions (could be atomic or molecular orbitals, or sums and/or products thereof,) ψ_1 and ψ_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 ψ_1 and ψ_2 are energy eigenfunctions (or molecular orbitals) they must have different energies (except in rare cases of accidental degeneracy) if they have different symmetry.

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If ψ_1 and ψ_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 φ_1, φ_2, φ_3 .... φ_n. The representative matrix for a given symmetry operation, $\mathcal{O}_i$, is generated by operating on each of the n functions.

Thus, if
$$\mathcal{O}_i \varphi_1 = a^i_{11} \varphi_1 + a^i_{12} \varphi_2 + \ldots + a^i_{1n} \varphi_n$$

$$\mathcal{O}_i \varphi_2 = a^i_{21} \varphi_1 + a^i_{22} \varphi_2 + \ldots + a^i_{2n} \varphi_n$$

$$\vdots$$

$$\mathcal{O}_i \varphi_n = a^i_{n1} \varphi_1 + a^i_{n2} \varphi_2 + \ldots + a^i_{nn} \varphi_n$$

the matrix representing Θ_i is

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

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. <u>What is meant by irreducible?</u>

Example:

If two functions are a basis for a 2–dimensional <u>irreducible</u> representation, this means there is <u>no way</u> 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: $\quad \Theta_i p_x = a_{11}^i p_x + a_{12}^i py$

and $\quad \Theta_i p_y = a_{21}^i p_x + a_{22}^i py \quad$ for each operation Θ_i.

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The representation (i.e. the set of 2 x 2 matrices R_i is <u>reducible</u> if one can find new linear conbinations:

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

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

such that

$$\Theta_i' p_1 = p_1 \quad \text{or} \quad \Theta_i' p_1 = -p_1$$

and $\qquad \Theta_i' p_2 = p_2 \quad \text{or} \quad \Theta_i' p_2 = -p_2 \qquad$ for every Θ_i'.

In other words, if we cannot find linear combinations of p_x and p_y which simply go into + or – themselves for <u>each operation of the group</u> then p_x and p_y are a basis for a 2–dimensional irreducible representation of the group.
(See pages 96–97 in text).

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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 invarient 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 dimensionsal	E
three dimensional	T (or F)
four dimensional	G
etc.	

Example: Character Table for the D_{6h} point group, to which benzene belongs
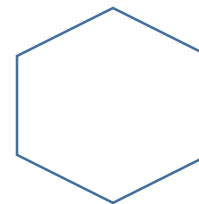
D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_g	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	(xz, 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, , and the p_x, p_y orbitals have E_{1u} symmetry
The dxy and dx²-y² d orbitals have E_{2g} symmetry, etc.