From the Gaussian16 Website  http://gaussian.com/keywords/  564-19 Lec20  Wed 27feb19

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. Other software packages with DFT facilities use the equivalent of SVWNs 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: Slater exchange, $p^2/3$ with theoretical coefficient of 2/3, also referred to as Local Spin Density exchange [Hohenberg64, Kohn65, Slater74]. Keyword if used alone: HFS.
- S: Slater exchange, $p^2/3$ 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: xS.
- B: Becke’s 1988 functional, which includes the Slater exchange along with corrections involving the gradient of the density [Becke88b]. Keyword if used alone: FBK.
- M06L: Grimme’s functional including dispersion [Grimme06, Grimme11].
- B97D: Grimme’s functional including dispersion [Grimme06, Grimme11].
- tHCTH: Handy’s family of functionals including gradient-corrected correlation [Hamprecht08, Boese00, Boese01].
- PBE: The 1996 functional of Perdew, Burke and Ernzerhof [Perdew96a, Perdew97].
- O: Handy’s OPTX modification of Becke’s exchange functional [Handy01].
- 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, Kohn, 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).
- VWN: 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, Mishchich89].
- PL (Perdew Local): The local (non-gradient corrected) functional of Perdew (1981) [Perdew81].
- P86 (Perdew 86): The gradient corrections of Perdew, along with his 1981 local correlation functional [Perdew86].
- BV55 (Becke 95): Becke’s $\tau$-dependent gradient-corrected correlation functional [Becke95].
- B95: The 1996 gradient-corrected correlation functional of Perdew, Burke and Ernzerhof [Perdew96a, Perdew97].
- TPSS: The t-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].
- BRx: Becke-Roussel correlation functional [Becke89a].
- PKZB: The correlation part of the Perdew, Kohn, Zupan and Blaha functional [Perdew99].
- VLYP: VWN5 local and P86 non-local correlation functional.
- VSX: van Vosk and Scuseria’s $\tau$-dependent gradient-corrected correlation functional [VanVoorhis98].
- HCTH: Handy’s family of functionals including gradient-corrected correlation [Hamprecht08, 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.
- B97D: Grimme’s functional including dispersion [Grimme06]. B97D3 requests the same but with Grimme’s D3BJ dispersion [Grimme11].
- M06: [Zhao06a], SOGGA11 [Peverati11], M11 [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 Trace 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,
- a reflection through a plane passing through the center,
- 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.
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 $\psi_1$ and $\psi_2$ 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 $\psi_1$ and $\psi_2$ "have different symmetry", i.e., 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.)
irreducible representation matrices remain \textbf{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.
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?

- $1s$
- $2p_y$
- $C_4^+ 2p_y$
- $C_2 2p_y$
If $A=B=C=D$, would say object is in C4 point group “C4 symmetry”

C4 Character (Eigenvalue) Table

<table>
<thead>
<tr>
<th></th>
<th>C4</th>
<th>C4$^+$</th>
<th>C4$^-$</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

**E** Character (Eigenvalue) Table

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>C4</th>
<th>C2</th>
<th>(C4)$^3$</th>
<th>linear, rotations</th>
<th>quadratic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$z, R_z$</td>
<td>$x^2+y^2, z^2$</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>$x^2-y^2, xy$</td>
</tr>
<tr>
<td><strong>E</strong></td>
<td>1</td>
<td>i</td>
<td>-1</td>
<td>-i</td>
<td>$x+iy; R_x+iR_y$</td>
<td>(yz, xz)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-i</td>
<td>1</td>
<td>i</td>
<td>$x-iy; R_x-iR_y$</td>
<td></td>
</tr>
</tbody>
</table>

**I and C2**

**C4$^+$ and C4$^-$**
### Group $C_3$ Multiplication Table

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>$C_3^+$</th>
<th>$C_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I</td>
<td>$C_3^+$</td>
<td>$C_3^-$</td>
</tr>
<tr>
<td>$C_3^+$</td>
<td>$C_3^+$</td>
<td>$C_3^-$</td>
<td>I</td>
</tr>
<tr>
<td>$C_3^-$</td>
<td>$C_3^-$</td>
<td>I</td>
<td>$C_3^+$</td>
</tr>
</tbody>
</table>

**Diagrams:**

- **1s**
- **2$p_y$**
- **$C_3^+ 2p_y$**
- **$C_3^- 2p_y$**
## Group $C_3$ Character Table

<table>
<thead>
<tr>
<th></th>
<th>$C_3^+$</th>
<th>$C_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
</tr>
</tbody>
</table>

- **A**
  - $C_3^+$: 1
  - $C_3^-$: 1
  - $z$
  - $z^2, x^2+y^2$

- **E**
  - $C_3^+$: 2
  - $C_3^-$: -1
  - $x,y$
  - $x^2-y^2$

---

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 \( p_y \)

\[
I \begin{pmatrix} p_x \\ p_y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix}
\]

The character = the trace = 2

Consider the effect of applying \( C_3^+ (120^0 \text{ CW rotation}) \) to \( p_x \) and \( p_y \)

\[
C_3^+ \begin{pmatrix} p_x \\ p_y \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} p_x + \frac{\sqrt{3}}{2} p_y \\ \sqrt{3} p_x + \frac{1}{2} p_y \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \sqrt{3} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix}
\]

The character = the trace = -1

That is exactly what the character table says for \( x,y \) which is what \( p_x \) and \( p_y \) are.

Thus, \( p_x \) and \( p_y \) belong to the \( E \) irreducible representation.

(E always indicates dimension = 2)
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,) \( \psi_1 \) 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,

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

(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 $\phi_1, \phi_2, \phi_3, \ldots, \phi_n$. The representative matrix for a given symmetry operation, $\Sigma_1$, is generated by operating on each of the $n$ functions.

   Thus, if $\Sigma_1 \phi_1 = a_{11}^i \phi_1 + a_{12}^i \phi_2 + \ldots + a_{1n}^i \phi_n$

   $\Sigma_1 \phi_2 = a_{21}^i \phi_1 + a_{22}^i \phi_2 + \ldots + a_{2n}^i \phi_n$

   $\vdots$

   $\Sigma_1 \phi_n = a_{n1}^i \phi_1 + a_{n2}^i \phi_2 + \ldots + a_{nn}^i \phi_n$
the matrix representing \( \Theta^i \) is

\[
R^i = \begin{pmatrix}
   a^i_{11} & a^i_{12} & \cdots & a^i_{1n} \\
   a^i_{21} \\
   a^i_{31} \\
   \vdots \\
   a^i_{n1} & a^i_{n2} & \cdots & a^i_{nn}
\end{pmatrix}
\]

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: \( \Theta^i_{1x} = a^i_{11}x + a^i_{12}y \)

   and \( \Theta^i_{1y} = a^i_{21}x + a^i_{22}y \) for each operation \( \Theta^i \).
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

\[
\Theta_i p_1 = p_1 \quad \text{or} \quad \Theta_i p_1 = -p_1
\]

and

\[
\Theta_i p_2 = p_2 \quad \text{or} \quad \Theta_i p_2 = -p_2 \quad \text{for every} \quad \Theta_i.
\]

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

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

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

The symbols in the two right-hand columns have the following meanings:
The position operators $x$, $y$, $z$, and the $p_x$, $p_y$ orbitals have $E_{1u}$ symmetry
The $dxy$ and $dx^2-y^2$ $d$ orbitals have $E_{2g}$ symmetry, etc.