

Symmetry-adapted linear combinations and other symmetry stuff

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- **Question:** *what is a group (in mathematical sense)?*
- A **group** G is a set for the elements of which an operation \cdot (“multiplication”) is defined such as:
 - $\forall a, b \in G, a \cdot b \in G$ (**closure**)
 - $\forall a, b, c \in G, (a \cdot b) \cdot c = a \cdot (b \cdot c)$ (**associativity**)
 - $\exists e: \forall a \in G, a \cdot e = e \cdot a = a$ (**identity**)
 - $\forall a \in G, \exists a^{-1}: a^{-1} \cdot a = a \cdot a^{-1} = e$ (**invertibility**)
- ▶ A group may or may not be *commutative (Abelian)*: $a \cdot b = b \cdot a$
- In chemistry, we usually consider the groups of *symmetry operations* \hat{R} acting in a 3-D vector space \mathbb{R}^3 : $\mathbf{r}' = \hat{R}\mathbf{r}$.
- ▶ Every closed(!) symmetry operation R is a linear transformation and can be represented by a 3×3 orthogonal (unitary) matrix $\Gamma(R)$.
- *Symmetry operations* retain the nuclei unaltered.
- **Question:** *why do they form a group?*
- *Symmetry operations*:
 - Closed: $E, C_n, S_n, \bar{n}, i, \sigma$.
 - Open: translations, screw axes, glide planes – never in molecules
- *Point groups*: those with closed operations only.

Closed symmetry operations

Identity E	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
Proper rotation C_n $\varphi = 2\pi/n$	$\begin{pmatrix} \cos \varphi & \sin \varphi & 0 \\ -\sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$
Improper rotation S_n	$\begin{pmatrix} \cos \varphi & \sin \varphi & 0 \\ -\sin \varphi & \cos \varphi & 0 \\ 0 & 0 & -1 \end{pmatrix}$
Rotoinversion \bar{n} equivalent to S_n for <u>even</u> n , equivalent to S_{2n} for <u>odd</u> n	$\begin{pmatrix} -\cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & -\cos \varphi & 0 \\ 0 & 0 & -1 \end{pmatrix}$
Inversion i	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
Reflection σ	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

A short symmetry quiz

- Find the point group of the following molecules

Molecule	Point group
BH ₃	
NH ₃	
CH ₄	
CCl ₄	
PtCl ₄ ²⁻	
PF ₅	
C ₆ H ₆ (benzene)	
C ₆ H ₃ F ₃ (1,3,5-trifluorobenzene)	

Point groups – multiplication table

- Example: $C_{2v} = \{E, C_2, \sigma_{xz}, \sigma_{yz}\}$

► Multiplication table:

	E $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	C_2 $\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	σ_{xz} $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	σ_{yz} $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

- The Hamiltonian \hat{H} and any symmetry operator \hat{R} commute: $\hat{H}\hat{R} = \hat{R}\hat{H}$
 - To understand this, one has to be more precise with the definitions. We need an \hat{R} defined in a space of functions (like \hat{H}). The formal definition is as follows:
$$\hat{R}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r}); \quad \hat{R}f(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = f(\hat{R}^{-1}\mathbf{r}_1, \hat{R}^{-1}\mathbf{r}_2, \dots, \hat{R}^{-1}\mathbf{r}_N)$$
- A non-degenerate wavefunction, upon a symmetry operator, either remains unaltered or changes the sign:

$$\hat{H}\Psi = E\Psi$$

$$\hat{R}\hat{H}\Psi = E\hat{R}\Psi$$

$$\hat{H}\hat{R}\Psi = E\hat{R}\Psi$$

$$\hat{H}(\hat{R}\Psi) = E(\hat{R}\Psi)$$

Thus, $\hat{R}\Psi$ is also an eigenfunction of \hat{H} , with the same energy! But Ψ is non-degenerate, hence $\hat{R}\Psi$ cannot be linearly independent. Thus, (in view of normalization) $\hat{R}\Psi = \Psi$ or $\hat{R}\Psi = -\Psi$.

- In a more “scientific” language, this reads as follows:

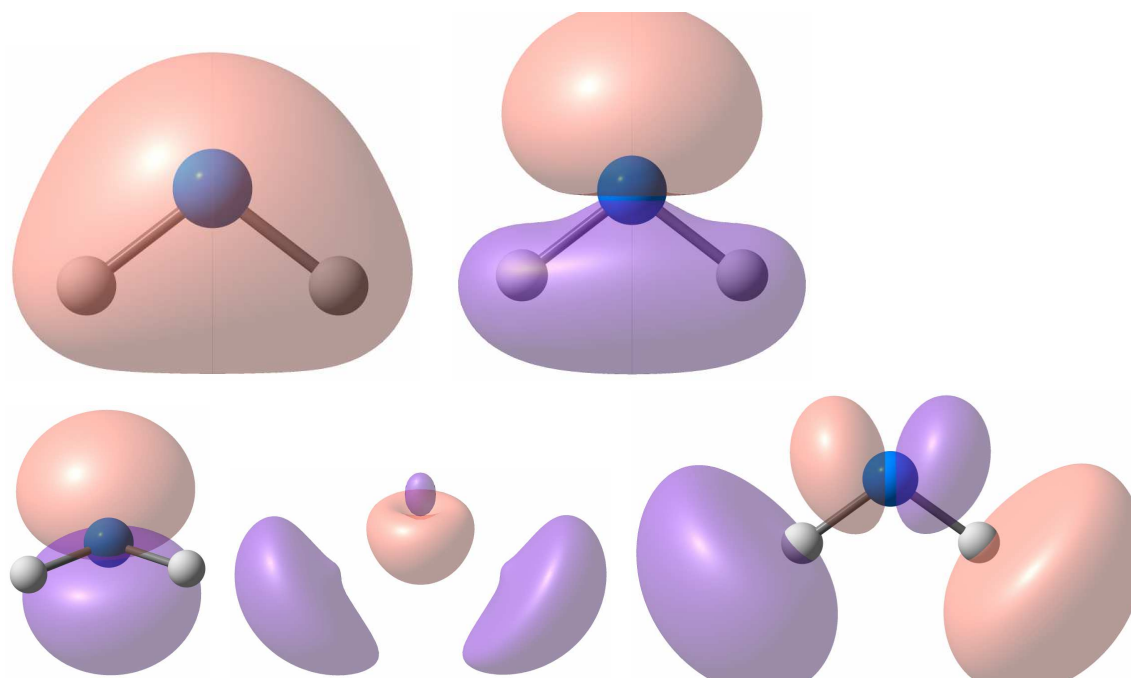
A non-degenerate wavefunction transforms under a one-dimensional irreducible representation of the molecular point group.

Point groups – why do we need representations?

- From the above, we see that a wavefunction (even a non-degenerate one) does not necessarily transform to itself upon acting of a symmetry operation. The information *how* it transforms is described by a *representation*.
 - For instance, a non-degenerate orbital can transform either to itself, or to *minus* itself: $\hat{R}\psi = \psi$ or $\hat{R}\psi = -\psi$.
 - If an orbital transforms to itself upon acting of *all* symmetry operations of the molecule ($\forall \hat{R}_i \in G, \hat{R}_i\psi = \psi$), it is called ***totally symmetric***.
- “An orbital transforms under *such-and-such* representation” – what does it mean? Easy for 1-D representations:
 - Example (C_{2v} group), 1-D representations:

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	s, p_z, d_{z^2}
A_2	1	1	-1	-1	d_{xy}
B_1	1	-1	1	-1	p_x, d_{xz}
B_2	1	-1	-1	1	p_y, d_{yz}

Exercise: attribute each of the MOs of the H_2O molecules to one of the representations



- A **representation** of a point group $G = \{\hat{R}_i\}$ is a set of matrices $\{\Gamma(\hat{R}_i)\}$, each of them corresponds to a group element ($\hat{R}_i \rightarrow \Gamma(\hat{R}_i)$) in such a way that $\Gamma(\hat{R}_i \hat{R}_j) = \Gamma(\hat{R}_i) \Gamma(\hat{R}_j)$. In other words, a representation has the same “multiplication table” as the group itself.

► The matrices $\Gamma(\hat{R}_i)$ and $\Gamma(\hat{R}_j)$ corresponding to different matrix elements, are not necessarily different: $\Gamma(\hat{R}_i) = \Gamma(\hat{R}_j)$ or $\Gamma(\hat{R}_i) \neq \Gamma(\hat{R}_j)$.

► The matrices can be of any dimension, including 1 (in which case they will be simply scalars). For a 1-D real representation,

$$\forall \hat{R}_i \in G, \Gamma(\hat{R}_i) = 1 \text{ or } \Gamma(\hat{R}_i) = -1.$$

$$\hat{R}_i \Psi = \Gamma(\hat{R}_i) \Psi, \quad \hat{R}_j \Psi = \Gamma(\hat{R}_j) \Psi, \quad \hat{R}_i \hat{R}_j \Psi = \hat{R}_i \Gamma(\hat{R}_j) \Psi = \Gamma(\hat{R}_j) \hat{R}_i \Psi = \Gamma(\hat{R}_j) \Gamma(\hat{R}_i) \Psi$$

Thus, acting by $\hat{R}_i \hat{R}_j$ is equivalent to multiplication by $\Gamma(\hat{R}_i) \Gamma(\hat{R}_j) = \Gamma(\hat{R}_i \hat{R}_j)$.

► Example (C_{2v} group), 1-D representations:

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	s, p_z, d_{z^2}
A_2	1	1	-1	-1	d_{xy}
B_1	1	-1	1	-1	p_x, d_{xz}
B_2	1	-1	-1	1	p_y, d_{yz}

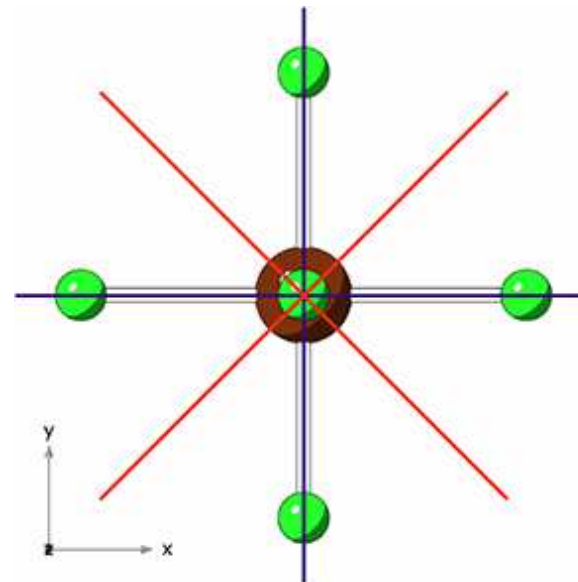
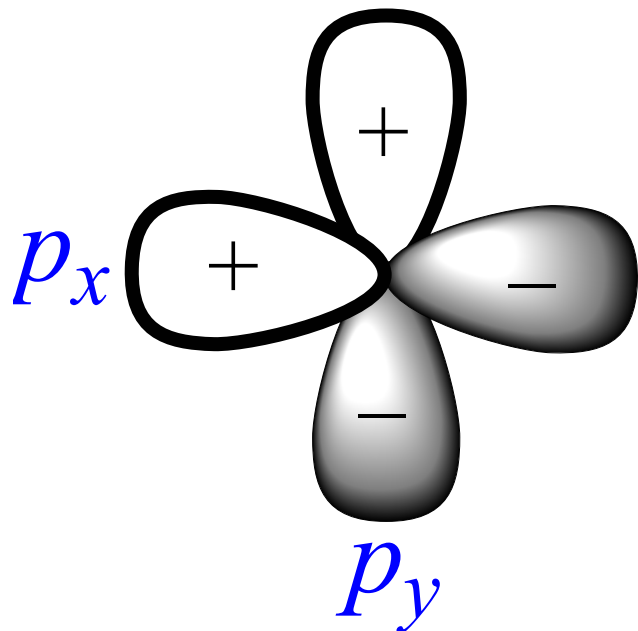
	E	C_2	σ_{xz}	σ_{yz}
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

Exercise: check this, looking at the multiplication table!

► Example (C_{4v} group), 2-D representation:

	E	$C_4(z)$	C_4^{-1}	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	σ_{d1}	σ_{d2}
E	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$

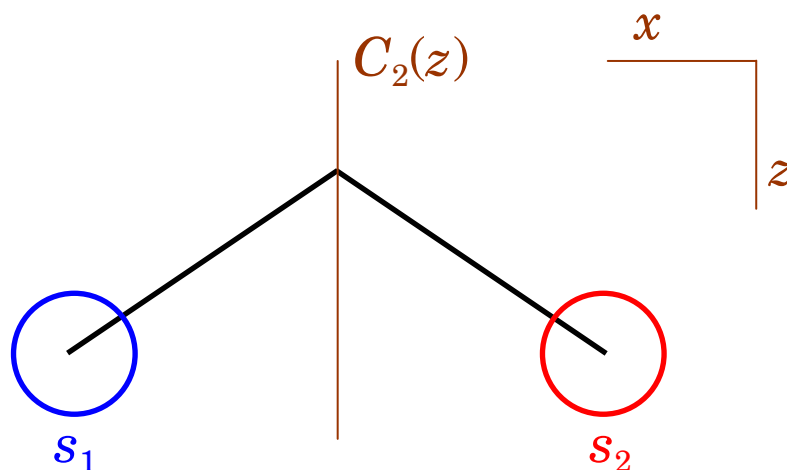
Exercise: consider the transformation of p_x and p_y orbitals. Construct the representation matrices for the $\sigma_v(xz)$, $\sigma_v(yz)$, σ_{d1} , σ_{d2} operations that are missing in the above table.



► If we apply a similarity transformation to all the above matrices, we get another *equivalent* representation. This means a change of the basis.

Point groups – reducible and irreducible representations

- Consider hydrogen s -orbitals in the H_2O molecule:



Exercise: How do they transform?

		Representation
$E(s_1) = s_1$	$E(s_2) = s_2$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$C_2(s_1) = s_2$	$C_2(s_2) = s_1$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$\sigma_{xz}(s_1) = s_1$	$\sigma_{xz}(s_2) = s_2$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\sigma_{yz}(s_1) = s_2$	$\sigma_{yz}(s_2) = s_1$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

This is a 2-D reducible representation!

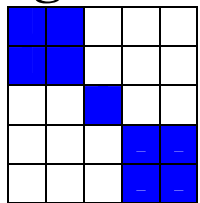
- A **reducible** representation: A 2-D representation $\{\Gamma(\hat{R}_i)\}$ is *reducible*, if we can find some matrix X such that all the matrices $\{X^{-1}\Gamma(\hat{R}_i)X\}$ are diagonal.
- In other words, we can find linear combinations of the basis functions (such as s_1 and s_2 in the above example), each of them transforms only through itself (without involving the other one). In the above example, these linear combinations are quite obvious:

$$\varphi_1 = s_1 + s_2 ; \quad \varphi_2 = s_1 - s_2 \quad X = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

		Repr.
$E(\varphi_1) = E(s_1 + s_2) = s_1 + s_2 = \varphi_1$	$E(\varphi_2) = E(s_1 - s_2) = s_1 - s_2 = \varphi_2$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$C_2(\varphi_1) = C_2(s_1 + s_2) = s_2 + s_1 = \varphi_1$	$C_2(\varphi_2) = C_2(s_1 - s_2) = s_2 - s_1 = -\varphi_2$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
$\sigma_{xz}(\varphi_1) = \sigma_{xz}(s_1 + s_2) = s_1 + s_2 = \varphi_1$	$\sigma_{xz}(\varphi_2) = \sigma_{xz}(s_1 - s_2) = s_1 - s_2 = \varphi_2$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\sigma_{yz}(\varphi_1) = \sigma_{yz}(s_1 + s_2) = s_2 + s_1 = \varphi_1$	$\sigma_{yz}(\varphi_2) = \sigma_{yz}(s_1 - s_2) = s_2 - s_1 = -\varphi_2$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

Now φ_1 transforms through φ_1 only; φ_2 through φ_2 only. All the matrices are diagonal, and the 2-D representation can be consider as a *direct sum* of two 1-D representations (A_1 and B_1 in our case). This was a 2-D reducible representation. We have *reduced* it to 1-D irreducible representations (*irreps*).

- ▶ The 2-D reducible representation of the C_{2v} group (see previous page 10) is quite different from the E representation of the C_{4v} group (page 9), which is *irreducible*. In the latter case, one cannot find a linear combination of the basis functions to get them to transform each one only through itself. In other words, one cannot diagonalize $\{\Gamma(\hat{R}_i)\} \rightarrow \{X^{-1}\Gamma(\hat{R}_i)X\}$ all the matrices $\Gamma(\hat{R}_i)$ by the same transformation X .
- ▶ 3-D, 4-D etc. reducible representations are not necessarily reduced to a *diagonal* form; sometimes it is a *block-diagonal* one:



A 5-D representation is reduced to 3 irreps: two 2-D and one 1-D.

A reducible representation is said to be a *direct sum* of irreps:

$$\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)} \oplus \dots \oplus \Gamma^{(n)}$$

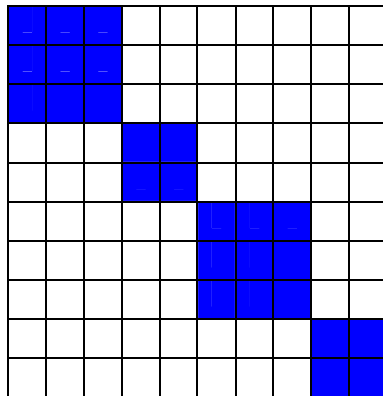
- ▶ Under a 1-D irrep, a single wavefunction (orbital) transforms; under a 2-D irrep, two orbitals transform jointly; under an N -dimensional irrep, N functions transform jointly.
- N -fold degenerate orbitals with a certain energy E transform jointly under an N -dimensional representation. Usually, this is an irrep, but in exceptional cases it can be a reducible representation (so-called “accidental degeneracy”).

- General remarks about the irreps:
 - ▶ Low-symmetry groups (C_1 , C_2 , C_i , C_s , C_{2h} , C_{2v} , D_2 , D_{2h} – those with a C_2 axis at most) have only 1-dimensional irreps.
 - ▶ Medium-symmetry groups (C_{3v} , D_{4h} , S_4 , D_{2d} – those with a single higher-order axis: C_3 , C_3, \dots or S_3 , S_4 (incl. the D_{2d} group) have 1-D and 2-D irreps. This is also true for linear groups $C_{\infty v}$ and $D_{\infty h}$.
 - ▶ High-symmetry groups (T , T_d , T_h , O , O_h , I , I_h – those with several non-coincident higher-order axes) have 1-D, 2-D, and 3-D irreps. The icosahedral groups I and I_h also have 4-D and 5-D irreps.
 - ▶ Irreps with dimensions higher than 5 are found only for the spherical group K_h and its subgroups.
 - ▶ The dimensionality of an irrep is related to the degeneracy of the molecular orbitals. For instance, in the D_{3h} group there are (among others) two 2-D irreps: E' and E'' . This means that there are some pairs of MOs e' and e'' . Such a pair of, e.g., e' orbitals transform together and is energetically degenerate. On the contrary, in a group with 1-D irreps only (e.g., C_{2v}) there are no degenerate orbitals (except by an improbable coincidence).

- There are simple ways of:
 - ▶ Reducing of a given reducible representation to irreducible;
 - ▶ Preparing a symmetry-adapted linear combinations of given basis functions; “*symmetry-adapted*” here means “*transforming under a certain irrep*”.
- The **advantage** of the symmetry-adapted basis functions is based on the following theorem regarding the Hamiltonian, overlap, and other similar matrix elements:

$$\int \varphi^{(\mu)}(\mathbf{r}) \hat{H} \varphi^{(\lambda)}(\mathbf{r}) d\mathbf{r} = 0; \quad \int \varphi^{(\mu)}(\mathbf{r}) \varphi^{(\lambda)}(\mathbf{r}) d\mathbf{r} = 0 \quad \text{etc. if } \mu \neq \lambda$$

That is, the matrix elements between the functions belonging to different irreps is always zero. Therefore, if we arrange the symmetry-adapted basis functions according to the irreps, Hamiltonian, overlap etc. matrices will have a block-diagonal shape:



Every block corresponds to one certain irrep. All the matrix elements outside the blocks are zero. The blocks can be treated (stored, diagonalized etc.) separately \Rightarrow great saving of computation time for integral calculation and for matrix manipulation.

- When MOs are formed, these symmetry-adapted linear combinations of basis functions (AOs) mix only within the irreps. Thus, to find all the a_1 MOs, we have to combine all possible symmetry-adapted basis functions of the same symmetry a_1 , and so on.

- Unlike the total Hamiltonian, the Fockian is not necessarily totally symmetric. Thus, it can be of lower symmetry, and the Hartree–Fock orbitals do *not necessarily* transform under an irrep of the molecular point group. See, e.g., the well-known example of the H_2 molecule at long H–H separations (UHF solution).
 - ▶ In such cases, we still can *force* the orbitals to be symmetric. Then the resulting Hartree–Fock energy will be higher.
 - ▶ Löwdin's *symmetry dilemma* is the choice between enforcing symmetric orbitals (possibly sacrificing energy) and allowing asymmetric orbitals (possibly gaining energy, but sacrificing symmetry: “symmetry breaking”).
 - A broken-symmetry solution of the Hartree–Fock or Kohn–Sham equation does not always exist. Often broken-symmetry initial guess will converge to “normal” MOs (i.e. those that transform under a irrep)
 - A broken-symmetry solution is most likely to be found for situation of non-equilibrium geometries (stretched bonds and so on), but not only.

- A **character** of a representation: the *trace* of the representation matrix:

$$\chi^{(\lambda)}(\hat{R}_i) = \sum_{k=1}^{l_\lambda} \Gamma^{(\lambda)}(\hat{R}_i)_{kk}$$

- ▶ For a 1-D representation, the character and the representation itself is the same.
 - ▶ Equivalent representations have the same characters. This is because the matrices $\Gamma(\hat{R}_i)$ and $X^{-1}\Gamma(\hat{R}_i)X$ have the same traces.
- The character of **reducible** representation is the sum of the characters of the irreps.

- A **reducible** representation is a *direct sum* of irreps:

$$\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)} \oplus \dots \oplus \Gamma^{(n)}$$

In terms of characters, it can be expressed as follows:

$$\chi^\Gamma(\hat{R}) = \sum_{\mu} a_{\mu} \chi^{(\mu)}(\hat{R})$$

- A method of obtaining the coefficients a_{μ} is explained on the following pages.

- **Orthogonality relation (Wigner's "Great orthogonality theorem", Schur's orthogonality relation):**

$$\sum_{R \in G} \Gamma^{(\lambda)}(R)_{nm}^* \Gamma^{(\mu)}(R)_{n'm'} = \delta_{\lambda\mu} \delta_{nn'} \delta_{mm'} \frac{|G|}{l_\lambda}$$

where $\Gamma^{(\mu)}(R)_{nm}$ is the matrix element nm of the irrep μ for the symmetry element R . $|G|$ is the order (number of the elements) of the group. l_λ is the dimension of representation λ . *Only valid for irreducible representations!*

- Corollary (much more important than the theorem itself):

► Orthogonality of characters:

$$\sum_{R \in G} \chi^{(\lambda)}(R)^* \chi^{(\mu)}(R) = \delta_{\lambda\mu} |G|$$

***Exercise:** Prove this corollary!*

► Example (C_{4v} group), 2-D representations:

	E	$2C_4(z)$	$C_2(z)$	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

$2C_4$ means C_4 and C_4^{-1} ;

$2\sigma_v$ means $\sigma_v(xz)$ and $\sigma_v(yz)$;

$2\sigma_d$ means two other symmetry planes (the "diagonal" ones)

Character theory (excerpts)

- A method of obtaining the coefficients a_μ (owing to the orthogonality of characters) to reduce a reducible representation (Γ) to irreps (μ):

$$a_\mu = \frac{1}{|G|} \sum_{R \in G} \chi^\Gamma(R) \chi^{(\mu)}(R)$$

Exercise: Reduce the 2-D representation of the C_{2v} group from page 10 using the character theory.

		Representation
$E(s_1) = s_1$	$E(s_2) = s_2$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$C_2(s_1) = s_2$	$C_2(s_2) = s_1$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$\sigma_{xz}(s_1) = s_1$	$\sigma_{xz}(s_2) = s_2$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\sigma_{yz}(s_1) = s_2$	$\sigma_{yz}(s_2) = s_1$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

Note: it is not necessary to construct entire representation matrices in order to figure out the characters (*think!*)

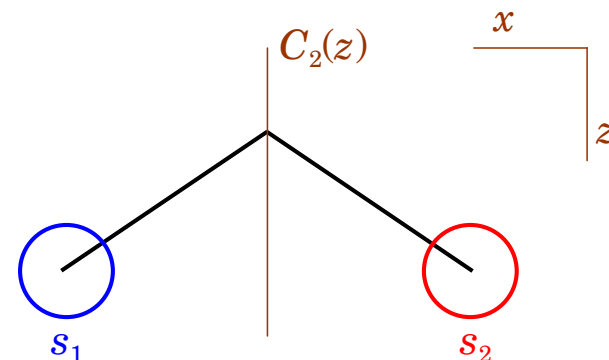
	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

- Symmetry-adapted basis: Projection onto an irrep μ :

$$\hat{P}^{(\mu)} = \frac{l_\mu}{|G|} \sum_{R \in G} \chi^{(\mu)}(R) \hat{R}$$

- Projection of a function $f(\mathbf{r})$ onto an irrep μ :

$$\hat{P}^{(\mu)} f(\mathbf{r}) = \frac{l_\mu}{|G|} \sum_{R \in G} \chi^{(\mu)}(R) \hat{R} f(\mathbf{r})$$



- The projector $\hat{P}^{(\mu)}$ should be applied to all irreps and all basis functions. In some cases it will result to the same projections, or the result may be zero. In total, from N basis functions we will obtain exactly N different symmetry-adapted linear combinations. This procedure works both for 1-D and 2-D and higher-dimension representations.

Exercise: Project a hydrogen s function onto each of the irreps of the C_{2v} group in H_2O .

$$\varphi_1 = \hat{P}^{A_1}(s_1) = \frac{1}{4}(1 \cdot E(s_1) + 1 \cdot C_2(s_1) + 1 \cdot \sigma_{xz}(s_1) + 1 \cdot \sigma_{yz}(s_1)) = \frac{1}{4}(s_1 + s_2 + s_1 + s_2) = \frac{1}{2}(s_1 + s_2)$$

$$\hat{P}^{A_2}(s_1) = \frac{1}{4}(1 \cdot E(s_1) + 1 \cdot C_2(s_1) - 1 \cdot \sigma_{xz}(s_1) - 1 \cdot \sigma_{yz}(s_1)) = \frac{1}{4}(s_1 + s_2 - s_1 - s_2) = 0$$

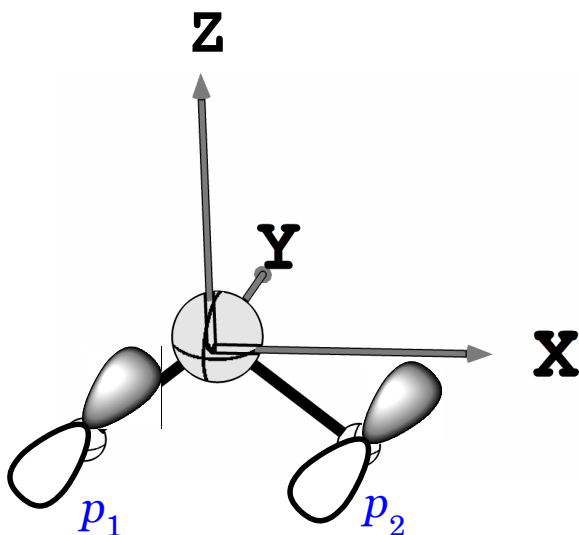
$$\varphi_2 = \hat{P}^{B_1}(s_1) = \frac{1}{4}(1 \cdot E(s_1) - 1 \cdot C_2(s_1) + 1 \cdot \sigma_{xz}(s_1) - 1 \cdot \sigma_{yz}(s_1)) = \frac{1}{4}(s_1 - s_2 + s_1 - s_2) = \frac{1}{2}(s_1 - s_2)$$

$$\hat{P}^{B_2}(s_1) = \frac{1}{4}(1 \cdot E(s_1) - 1 \cdot C_2(s_1) - 1 \cdot \sigma_{xz}(s_1) + 1 \cdot \sigma_{yz}(s_1)) = \frac{1}{4}(s_1 - s_2 - s_1 + s_2) = 0$$

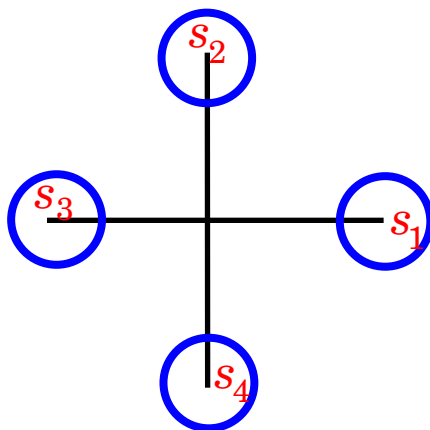
If we act by those projectors on the s_2 function, we get the same linear combinations.

Exercise: Obtain molecular orbitals of H_2O by combining φ_1 and φ_2 with suitable AOs of the oxygen

Exercise: Project hydrogen p_y function onto each of the irreps of the C_{2v} group in H_2O . Do a similar **exercise** with hydrogen p_x functions, as well as with some of the d functions (Recall the shape of the d orbitals!)



Exercise: Obtain symmetry-adapted linear combinations from the four s orbitals shown below (C_{4v} group).



Note. To project on a 2-D representation, use two linearly independent functions.

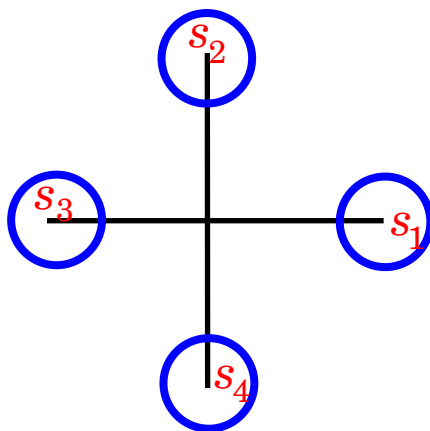
► C_{4v} group. **Exercise:** Compare the C_{4v} character table with that for the C_4 group. You will find something remarkable!

C_{4v}	E	$C_4(z)$	$C_4^{-1}(z)$	$C_2(z)$	σ_{v1}	σ_{v2}	σ_{d1}	σ_{d2}
A_1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1	-1	-1
B_1	1	-1	-1	1	1	1	-1	-1
B_2	1	-1	-1	1	-1	-1	1	1
E	2	0	0	-2	0	0	0	0

Exercise: Prepare symmetry adapted atomic orbitals for H_2O .

Exercise: Obtain molecular orbitals of I_3^- . Take the C_2 or C_s group for simplicity. Take into account that σ - and π -orbitals do not mix.

- **Orbital correlation and splitting.** Imagine we have a molecule of C_{4v} symmetry. It has, in general, some a_1 , a_2 , b_1 , b_2 , and e molecular orbitals (e orbitals are degenerate). Let us *stretch* the molecule along the x axis. It will now have a C_{2v} symmetry only. The question is, which symmetry the former a_1 , a_2 , b_1 , b_2 , and e orbitals will have. Obviously a different one, because those representations do not exist in the C_{2v} group.



Example (C_{4v} group), 2-D representations:

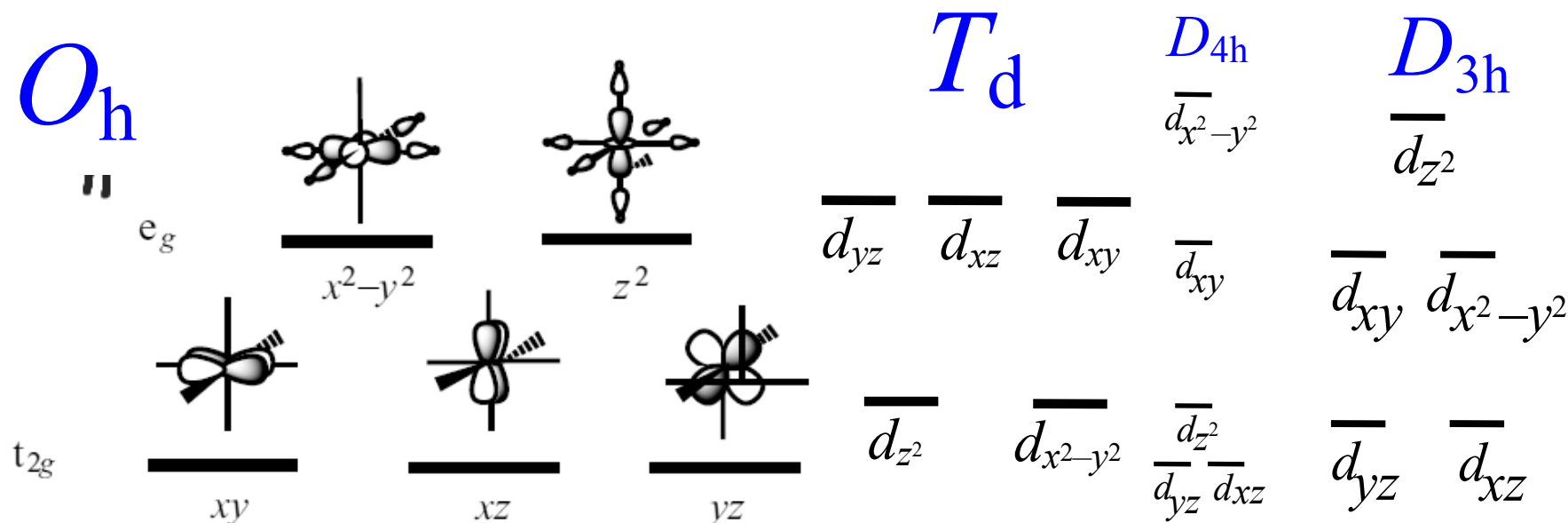
C_{4v}	E	$C_4(z)$	$C_4^{-1}(z)$	$C_2(z)$	σ_{v1}	σ_{v2}	σ_{d1}	σ_{d2}
A_1	1	1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1	-1	-1
B_1	1	-1	-1	1	1	1	-1	-1
B_2	1	-1	-1	1	-1	-1	1	1
E	2	0	0	-2	0	0	0	0

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

$A_1 \rightarrow A_1$; $A_2 \rightarrow A_2$; $B_1 \rightarrow A_1$; $B_2 \rightarrow A_2$; $E \rightarrow B_1 \oplus B_2$ (this one is a Jahn–Teller splitting!)

- **Crystal field splitting.** Imagine we have a spherical atom surrounded by point charges of a lower symmetry (e.g., O_h). According to the *degenerate perturbation theory*, the orbital energies of the perturbed Hamiltonian are *eigenvalues* of the perturbation operator that has the O_h symmetry. The effect is the orbital splitting.

Octahedral field – O_h splitting: $D \rightarrow T_{2g} \oplus E_g$.



Tetrahedral field – T_d splitting: $D \rightarrow T_2 \oplus E$.

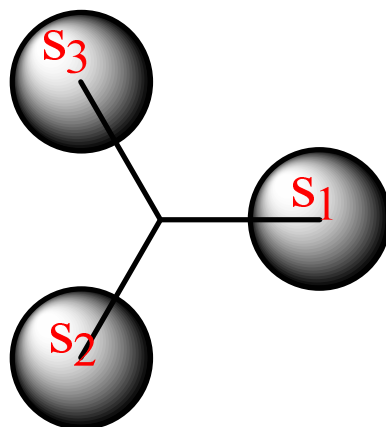
Square planar field – D_{4h} splitting: $D \rightarrow A_{1g} \oplus B_{1g} \oplus B_{2g} \oplus E_g$

O_h splitting $T_{2g} \rightarrow B_{2g} \oplus E_g$; $E_g \rightarrow A_{1g} \oplus B_{1g}$

Trigonal bipyramidal field – D_{3h} splitting: $D \rightarrow A_1 \oplus E' \oplus E''$

Character theory (excerpts)

Exercise: Consider three 1s orbitals of hydrogen atoms in BH_3 . Take the C_{3v} or D_3 group or for simplicity. Prepare symmetry-adapted linear combinations from the hydrogen 1s orbitals.



$$\begin{aligned}\varphi_1 = \hat{P}^{A_1}(s_1) &= \frac{1}{6} (1 \cdot E(s_1) + 1 \cdot C_3(s_1) + 1 \cdot C_3^{-1}(s_1) + 1 \cdot \sigma_1(s_1) + 1 \cdot \sigma_2(s_1) + 1 \cdot \sigma_3(s_1)) = \\ &= \frac{1}{6} (s_1 + s_2 + s_3 + s_1 + s_3 + s_2) = \frac{1}{3} (s_1 + s_2 + s_3)\end{aligned}$$

$$\varphi_2 = \hat{P}^E(s_1) = ?$$

$$\varphi_3 = \hat{P}^E(s_2) = ?$$

C_{3v}	E	C_3	C_3^{-1}	σ_1	σ_2	σ_3
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0