Permutation and Unitary Symmetries of Many-Electron Wavefunctions

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Introduction: Schrödinger equation

Basic problem of quantum chemistry (electronic structure):

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

with

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,A}\frac{Z_A}{r_{iA}}}_{\sum_i \hat{h}_i} + \sum_{i>j}\frac{1}{r_{ij}} + \sum_{A>B}\frac{Z_A Z_B}{r_{AB}}$$

where A, B and i, j are nuclear and electronic indices, respectively. Z stands for nuclear charge, r for the distance of the particles.

Introduction: Schrödinger equation

Basic problem of quantum chemistry (electronic structure):

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

Important properties of the wave functions:

- spin
- spatial symmetry

Introduction: Schrödinger equation

Basic problem of quantum chemistry (electronic structure):

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

- spin: $\hat{H}\hat{S}_z = \hat{S}_z\hat{H}$ and $\hat{H}\hat{S}^2 = \hat{S}^2\hat{H}$
- spatial symmetry: $\hat{H}\hat{R} = \hat{R}\hat{H}$

Therefore:

- Ψ will also be eigenfunction of spin and spatial symmetry
- Ψ can be labeled by spin quantum number and properties associated with spatial symmetry

Introduction: How to construct wave function?

1) *Product wave function* (antisymmetrized by $\mathcal{A}$):

$$\Psi(1,2,3,...,n) \quad = \quad \mathcal{A}(\phi_1(1)\cdot\phi_2(2)\cdot\phi_3(3)\cdot...\cdot\phi_n(n))$$

To construct products which have the correct spin and spatial properties, we need to know:

- spin properties of products of spin functions
- spatial symmetry of products of spatial functions

Introduction: How to construct wave function?

2) *Wave function by linear combinations:*

$$\Psi = \sum_i c_i \Phi_i$$

There are two ways to construct linear combinations with the correct spin and spatial properties:

- obtain coefficients which results in proper spin and spatial properties
- use basis functions which have already proper spin and spatial properties (*CSF: Configuration State Function*)

Introduction: Block structure of the Hamiltonian

Advantage of using eigenfunctions of a commuting operator $\hat{A}$ as a basis:

If $[\hat{H}, \hat{A}] = 0$, and the basis $\{\Phi_i\}$ consists of the eigenfunctions of $\hat{A}$:

$$\hat{A}\Phi_j^{a_i} = a_i \Phi_j^{a_i}$$

then the matrix of $\hat{H}$ is block diagonal in this basis:

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}^{a_1} & 0 & 0 & \vdots \\ 0 & \mathbf{H}^{a_2} & 0 & \vdots \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & \mathbf{H}^{a_n} \end{pmatrix}$$

with $\mathbf{H}^{a_i}$ is the block belonging to functions $\{\Phi_j^{a_i}\}$ with eigenvalue a_i.

The wave function in this block:

$$\Psi^{a_i} = \sum_j c_j \Phi_j^{a_i}$$

Introduction: Calculation of matrix elements

$$H_{ij} \quad = \quad \langle \Phi_i | \hat{H} | \Phi_j \rangle$$

One can simplify the calculations if we know the spin and spatial properties of the matrix elements.

Introduction: Second quantization

The Hamiltonian:

$$\hat{H} = \sum_{rs} h_{rs}\hat{E}_{rs} + \frac{1}{2}\sum_{rstu}\langle rt|su\rangle[\hat{E}_{rs}\hat{E}_{tu} - \delta_{st}\hat{E}_{ru}]$$

where

$$h_{rs} = \int \phi_r(1)\hat{h}(1)\phi_s(1)dv(1)$$

$$\langle rt|su\rangle = \int\int \phi_r^*(1)\phi_t^*(2)\frac{1}{r_{12}}\phi_s(1)\phi_u(2)dv(1)\ dv(2)$$

$$\hat{E}_{rs} = \hat{a}^\dagger_{r\alpha}\hat{a}_{s\alpha} + \hat{a}^\dagger_{r\beta}\hat{a}_{s\beta}$$

with $\hat{a}^\dagger$ and $\hat{a}$ being creation and annihilation operators.

An important property of the basic operators:

$$[\hat{E}_{rs}, \hat{E}_{tu}] = \delta_{st}\hat{E}_{ru} - \delta_{ru}\hat{E}_{ts}$$

Introduction: Second quantization

Matrix element:

$$\begin{aligned} H_{ij} &= \langle \Phi_i | \hat{H} | \Phi_j \rangle \\ &= \sum_{rs} h_{rs} \langle \Phi_i | \hat{E}_{rs} | \Phi_j \rangle + \frac{1}{2} \sum_{rstu} \langle rt | su \rangle \left[\langle \Phi_i | \hat{E}_{rs} \hat{E}_{tu} | \Phi_j \rangle - \delta_{st} \langle \Phi_i | \hat{E}_{ru} | \Phi_j \rangle \right] \end{aligned}$$

All we need for the matrix elements are the

- integrals h_{rs} and $\langle rt | su \rangle$
- matrix elements of the basic operators (*coupling coefficients*).

The latter is a very sparse matrix.

Summary of introduction

Spin and spatial symmetry properties will be useful:

- to obtain spin and symmetry labels of atomic/molecular states
- to construct proper spin and symmetry eigenstates
- to calculate matrix elements

Introduction: plan of my talks

- basic group theory
- spatial symmetry and corresponding group theoretical terms
- permutation symmetry and the corresponding groups
- unitary group
- construction of spin eigenfunctions
- calculation of matrix elements
- symmetry properties of different wave functions

Recommended books/chapters

1. F. A. Cotton, *Chemical Application of Group Theory*, 2nd Edition, Wiley-Interscience, New York, 1973.

2. R. Pauncz, *Spin Eigenfunctions*, Plenum Press, New York, 1979.

3. I. Shavitt, *The Graphical Unitary Group Approach and Its Application to Direct Configuration Interaction Calculations The Unitary Group for the Evaluation of Electronic Energy Matrix Elements*, Ed. J. Hinze, Lecture Notes in Chemistry, Vol. 12, pg. 51-99, Springer, 1981.

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Basic Terms of Group Theory

Basic Terms of Group Theory

A *group* is a collection of *elements* which are interrelated by an *operation*:

$$A \cdot B \quad = \quad C$$

The following rules must be obeyed:

- set $\mathcal{G}$ is *closed* under the operation:
  if $A, B \in \mathcal{G}$ then $C \in \mathcal{G}$

- there must be a *unit element* (E, identity) such that:
  $E \cdot A = A \cdot E = A$

- multiplication is *associative*:
  $A \cdot (B \cdot C) = (A \cdot B) \cdot C$

- all elements must have its *reciprocal* (A^{-1}) in the group:
  $A \cdot S = S \cdot A = E \qquad\qquad S \equiv A^{-1}$

Basic Terms of Group Theory

Multiplication is not necessarily commutative:

$$A \cdot B \quad \neq \quad B \cdot A$$

Abelian group: If multiplication of any pair of elements *is* commutative.

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Abelian group: If multiplication of any pair of elements *is* commutative.

Dimension of the group (h):

- *finite group*: $h < \infty$
- *infinite group*: $h = \infty$

Basic Terms of Group Theory

Group multiplication table:

	A	B	C	D
A	A	B	C	D
B	B	A	D	C
C	C	D	A	B
D	D	C	B	A

Properties:

- each element appears only once in each row and column
- multiplication is single valued

Basic Terms of Group Theory

Group multiplication table:

	A	B	C	D
A	A	B	C	D
B	B	A	D	C
C	C	D	A	B
D	D	C	B	A

Properties:

- each element appears only once in each row and column
- multiplication is single valued

Subgroup: if a subset of elements obey the definition of a group, i.e. multiplication does not leed out of the group.

It must always include E, and of course the invers of all elements.

Basic Terms of Group Theory

Conjugate elements: A and B are conjugate to each oder, if

- $A, B, X \in \mathcal{G}$ and
- $B = X^{-1} \cdot A \cdot X$

Properties:

- If A is conjugate to B than B must be conjugate to A, i.e. the group must have an element Y such that:
  $A = Y^{-1} \cdot B \cdot Y$
- If A is conjugate to B and C then B and C are also conjugate to A.

Class: the complete set of elements which are conjugate to each other.

Basic Terms of Group Theory

Representation of a group

Remember the definitions: the group is defined by the multiplication table (relation of the elements) and not the individual property of the elements.

The same group can be also *represented* by:

- operators (e.g. symmetry operation – symmetry groups)
- permutations (permutation groups)
- ...
- matrices

Basic Terms of Group Theory

Assume a group with the following multiplication table:

	E	B	C	D
E	E	B	C	D
B	B	E	D	C
C	C	D	E	B
D	D	C	B	E

The following matrices obey the same multiplication table:

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{C} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{D} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Basic Terms of Group Theory

Assume a group with the following multiplication table:

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

The following matrices obey the same multiplication table:

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_v' = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Basic Terms of Group Theory

Representation of a group I

How many matrix representations can a group have?
. – As many as you just generate!!!

For example, by similarity transformation we get new set of matrices which also form a representation:

$$A' = L^{-1}AL \qquad B' = L^{-1}BL$$
$$A' \cdot B' \quad = \quad L^{-1}AL \cdot L^{-1}BL = L^{-1}A \cdot BL = L^{-1}CL = C'$$

Character of a representation:

By similarity transformation the character of a matrix[1] does not change
. → the character will be characteristic to the representation.

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[1] Sum of the diagonal elements; also called "spur" or "trace".

Basic Terms of Group Theory

Representation of a group II

Are there special ones among the representations?
. – Yes, these are the so called *irreducible representations*.

Irreducible representations:

- basic building blocks of representations
- any representation can be build up from these basic elements

Basic Terms of Group Theory

Representation of a group III

However, the name comes from a procedure starting at large matrices:

– assume we have a group represented by matrices $\mathbf{E}, \mathbf{B}, \mathbf{C}, \mathbf{D}, ...$

– we perform the same similarity transformation on all of them:

$$\begin{aligned} \mathbf{E}' &= \mathbf{L}^{-1}\,\mathbf{E}\,\mathbf{L} \\ \mathbf{B}' &= \mathbf{L}^{-1}\,\mathbf{B}\,\mathbf{L} \\ \mathbf{C}' &= \mathbf{L}^{-1}\,\mathbf{C}\,\mathbf{L} \end{aligned}$$

– similarity transformation does not change the multiplication rules
. → transformed matrices still give a representation (same character).

– Special transformation can lead to block diagonal matrices, e.g.:

$$\mathbf{B}' = \mathbf{L}^{-1}\mathbf{B}\mathbf{L} \quad = \quad \begin{pmatrix} \mathbf{B}'_1 & 0 & 0 & 0 & \cdots \\ 0 & \mathbf{B}'_2 & 0 & 0 & \cdots \\ 0 & 0 & \mathbf{B}'_3 & 0 & \cdots \\ 0 & 0 & 0 & \mathbf{B}'_4 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix}$$

– Block diagonal matrices can be multiplied block-wise:

$$\begin{aligned} \mathbf{B}'_1 \cdot \mathbf{C}'_1 &= \mathbf{D}'_1 \\ \mathbf{B}'_2 \cdot \mathbf{C}'_2 &= \mathbf{D}'_2 \\ &\vdots \end{aligned}$$

obeying the same multiplication rules

→ each block is a new representation.

Therefore:

If there exists a transformation which brings all matrices of a group to the same block structure, the representation can be split into "smaller" representations → i.e. the original representation *reducible*.

Note:

- the character of the representation is changed when it is splited into smaller pieces
- the sum of the character of new representations equals the character of the original representations

Notation: $\Gamma = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \cdots$

Irreducible representation:

- transformation leading simultaneously to block structure of the matrices does not exist

Basic Terms of Group Theory

How many *irreducible representations* of a group are there?

– One can show that the number of all irreducible representations equals to the number of the classes of the group.

Basic Terms of Group Theory

How many *irreducible representations* of a group are there?

– One can show that the number of all irreducible representations equals to the number of the classes of the group.

Character table:

Example: Character table of the C_{2v} point group

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

Rows correspond to the irreps and show the character of the elements (precisely: that of the classes).

Basic Terms of Group Theory

Basis of a representation

We know the relation between operators and matrices:

Consider a set of (linearly independent) functions $\{\phi_i\}$ such that the space spanned is an invariant space with respect to all operators of the group. E.g.:

$$\begin{aligned}
\hat{A}\phi_i &= \sum_j A_{ij}\phi_j \\
\hat{B}\phi_i &= \sum_j B_{ij}\phi_j \\
\hat{C}\phi_i &= \sum_j C_{ij}\phi_j \\
&\ldots
\end{aligned}$$

Basic Terms of Group Theory

Basis of a representation

The matrix representation of an operator in this basis can be given as:

$$A_{ij} \quad = \quad \langle \phi_i | \hat{A} | \phi_j \rangle$$

The matrices defined this way from operators belonging to a group, form also a group with the same multiplication table. It is said that the matrices $\mathbf{A}, \mathbf{B}, ...$ are the matrix representation of operators $\hat{A}, \hat{B}, ...$ on the basis $\{\phi_i\}$.

Notes:

- when transforming the matrices, in fact we transform the basis
- when finding the block diagonal form of the matrices and splitting up the representation accordingly, we divide up the space into smaller subspaces. Now the elements of subspaces will be used as basis of the representations.

Basic Terms of Group Theory

Reducing reducible representations

To split up reducible representations into irreducible ones, one can use the following formula:

$$n_i \quad = \quad \frac{1}{h}\sum_{k=1}^{r} N_k \, \chi^i(k) \, \chi(k)$$

with:

h: order of the group

N_k: order of the class

$\chi^i(k)$: character of kth class corresponding to irrep i

$\chi(k)$: character of kth class corresponding to the reducible representation

Basic Terms of Group Theory

To find the subspace spanning the irreducible representations, the following operator can be used, which projects into the space of the ith irrep:

$$\hat{P}_i \;=\; \sum_{\hat{R}} \chi^i(\hat{R})\, \hat{R}$$

with $\hat{R}$ being the element of the group, $\chi^i(\hat{R})$ being its character corresponding to the ith irrep.

Basic Terms of Group Theory

Reducing reducible representations

Example: Consider the water molecule in minimal basis.

Basis functions: H: $1\mathrm{s}_\mathrm{a}$, $1\mathrm{s}_\mathrm{b}$, O: 1s, 2s, $2\mathrm{p}_\mathrm{x}$, $2\mathrm{p}_\mathrm{y}$, $2\mathrm{p}_\mathrm{z}$

Character table for C_{2v} point group with the characters of the above representation:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
Γ_{basis}	7	1	3	5

Basic Terms of Group Theory

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
Γ_{basis}	7	1	3	5

$$n_i = \frac{1}{h} \sum_{k=1}^{r} N_k \, \chi^i(k) \, \chi(k)$$

$$\mathrm{n}_{\mathrm{A1}} = \frac{1}{4}(1 \cdot 1 \cdot 7 + 1 \cdot 1 \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot 5) = 4$$

$$\mathrm{n}_{\mathrm{A2}} = \frac{1}{4}(1 \cdot 1 \cdot 7 + 1 \cdot 1 \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot (-1) \cdot 5) = 0$$

$$\mathrm{n}_{\mathrm{B1}} = \frac{1}{4}(1 \cdot 1 \cdot 7 + 1 \cdot (-1) \cdot 1 + 1 \cdot 1 \cdot 3 + 1 \cdot (-1) \cdot 5) = 1$$

$$\mathrm{n}_{\mathrm{B2}} = \frac{1}{4}(1 \cdot 1 \cdot 7 + 1 \cdot (-1) \cdot 1 + 1 \cdot (-1) \cdot 3 + 1 \cdot 1 \cdot 5) = 2$$

Thus: Γ_{basis}=4 $\mathrm{A}_1 \oplus \mathrm{B}_1 \oplus 2\ \mathrm{B}_2$

This means, there are four a_1, one b_1 and two b_2 orbitals.

Basic Terms of Group Theory

Direct product representations

Consider two bases of representation $\{\phi_i\}$ and $\{\psi_i\}$:

$$\hat{A}\phi_i = \sum_j A^{\phi}_{ij}\phi_j \qquad \hat{A}\psi_i = \sum_j A^{\psi}_{ij}\psi_j$$

Then:

$$\hat{A}\phi_i\psi_j \quad = \quad \sum_k \sum_l A^{\phi}_{ik} A^{\psi}_{jl} \psi_k \phi_l$$

i.e. $\{\psi_i\psi_j\}$ also form a basis for the representation, that of the outer product of the two matrices:

$$\mathbf{A}^{\phi\otimes\psi} \quad = \quad \mathbf{A}^{\phi} \otimes \mathbf{A}^{\psi}$$

with $\mathbf{A}^{\phi\otimes\psi}$ having a dimension as product of the dimensions of the two representations.

Basic Terms of Group Theory

Direct product representations

Notation:

$$\Gamma^{\phi\otimes\psi} \quad = \quad \Gamma^{\phi} \otimes \Gamma^{\psi}$$

Character of the direct product representation:

The characters of the direct product representation are the products of the character of the representations forming the original representations.

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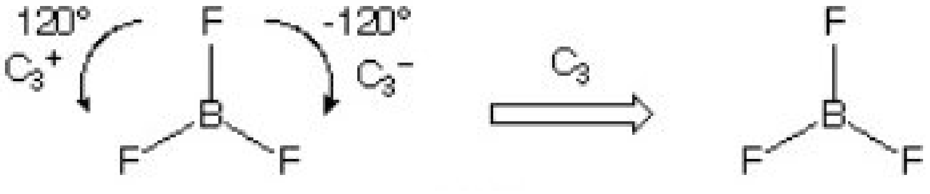
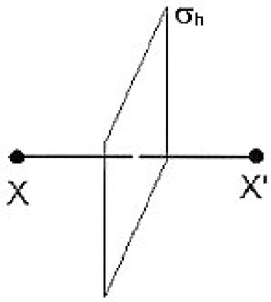
Spatial Symmetry of Molecules

Symmetry operations

- $\hat{C}_n$ – proper rotation (around the proper axis) by $2\pi/n$

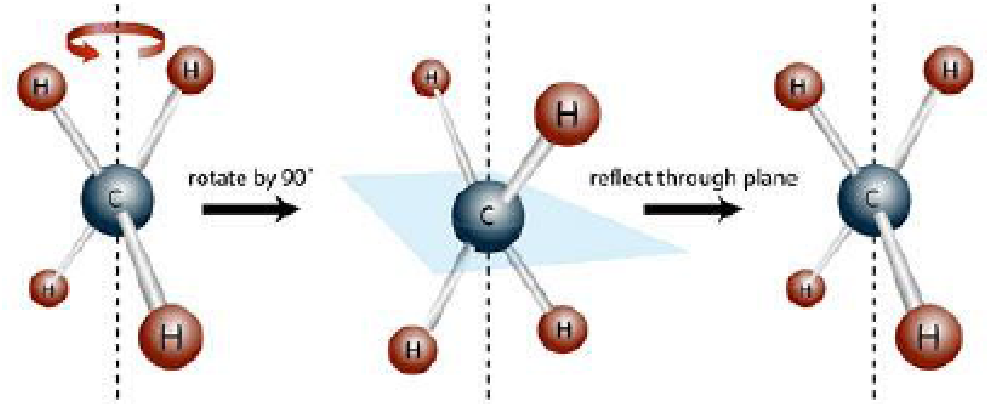


- $\hat{\sigma}$ – reflection (special cases: $\hat{\sigma}_v$, $\hat{\sigma}_h$, $\hat{\sigma}_d$)



Symmetry operations

- $\hat{S}_n$ – improper rotation: rotation ($\hat{C}_n$) followed by reflection in a plane perpendicular to the rotation axis (σ_h)



- $\hat{i}$ – inversion ($\hat{i} = \hat{S}_2$)

- $\hat{E}$ – unity: maps the object on itself (required only for mathematical purposes)

Point groups

Symmetry operations leaving an object (molecule) unchanged, form a group.

E.g. water (see next page):

Operators: $\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$

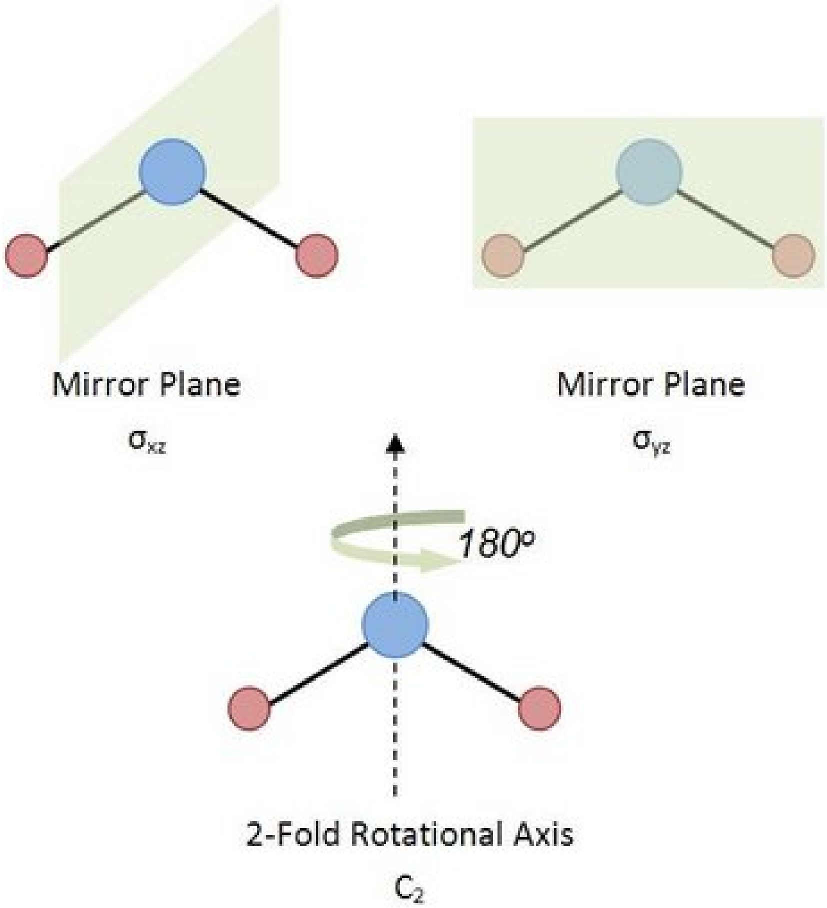
Multiplication table:

$\hat{C}_{2v}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	σ_v
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

The group formed by the symmetry operations is called the *point group*.

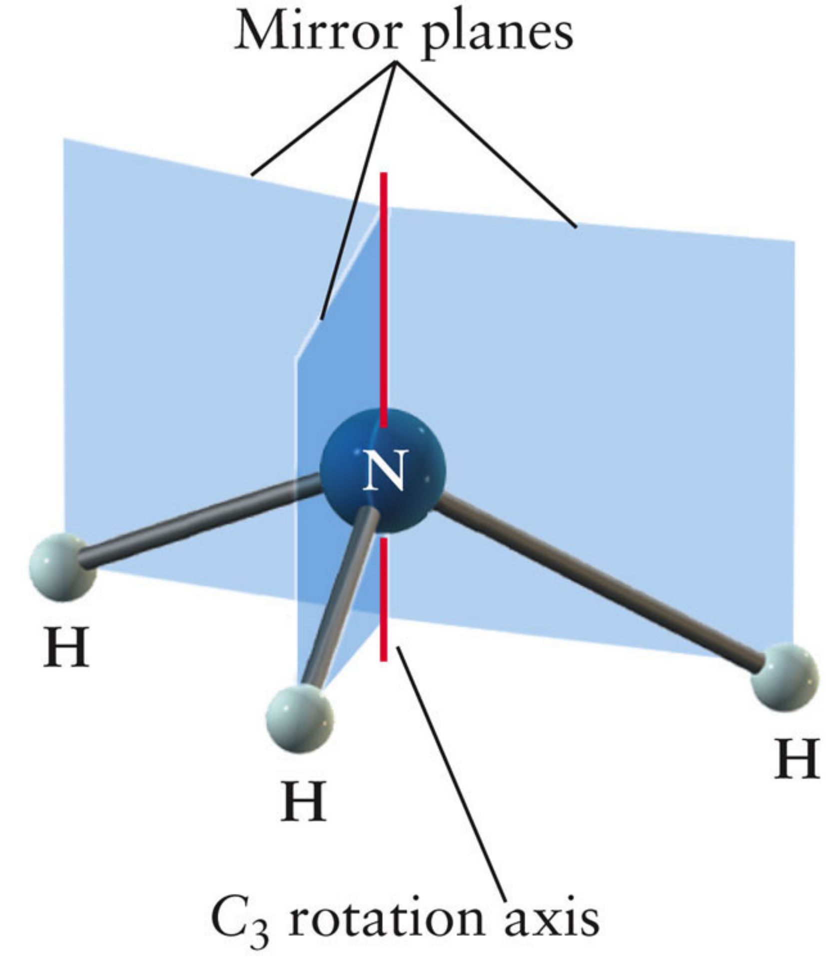
Point groups

Water: $\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$



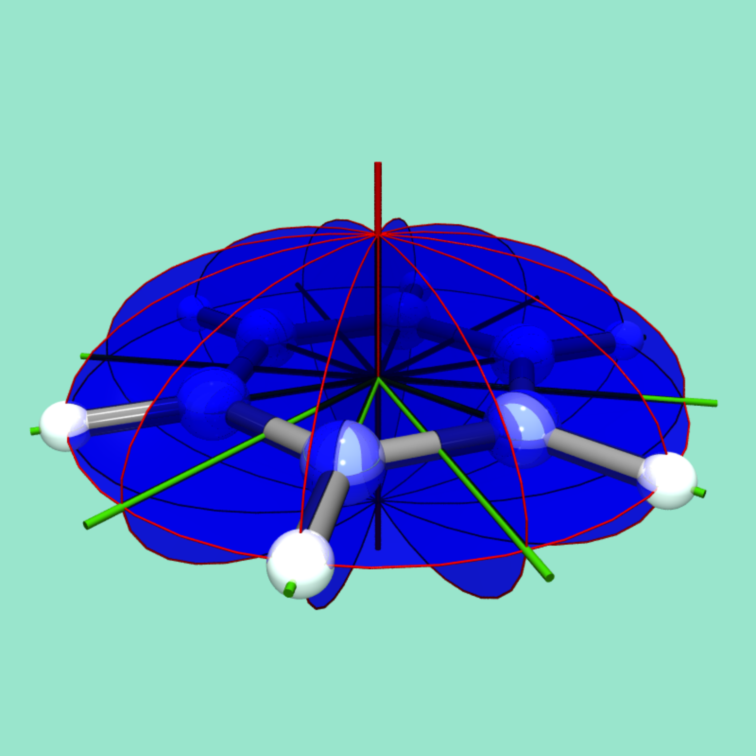
Point groups

Ammonia: $\hat{C}_3$, 3 times $\hat{\sigma}_v$, $\hat{E}$



Point groups

Benzene: $\hat{C}_6$, 6 times $\hat{C}_2$, $\hat{\sigma}_h$ (horizontal, perpendicular to the main axis), 6 times $\hat{\sigma}_v$ (including the main axis), $\hat{i}$, etc.



Generators of a group

Set of elements ($\mathcal{S}$) of the group $\mathcal{G}$ are called *generators* if all elements of $\mathcal{G}$ can be generated by multiplication of the elements of $\mathcal{S}$.

Example: benzene

Elements of the point group $\mathrm{D_{6h}}$:

$$\hat{E},\ 2\hat{C}_6,\ 2\hat{C}_3,\ \hat{C}_2,\ 3\hat{C}_2,\ 3\hat{C}_2,\ \hat{i},\ 2\hat{S}_6,\ 2\hat{S}_3,\ \hat{\sigma}_h,\ 3\hat{\sigma}_v,\ 3\hat{\sigma}_d$$

Three generators are able to produce these elements.

Set 1: $\hat{C}_6, \hat{C}_2'$ and $\hat{i}$.

$$\hat{C}_3 = \hat{C}_6 \cdot \hat{C}_6, \quad \hat{C}_2 = \hat{C}_6 \cdot \hat{C}_6 \cdot \hat{C}_6, \;\; \hat{C}_2" = \hat{C}_6 \cdot \hat{C}_2', \;\; \hat{\sigma}_v = \hat{C}_2' \cdot \hat{i} \text{ etc.}$$

Set 2: $\hat{C}_6$, $\hat{\sigma}_v$, $\hat{\sigma}_v$

Set 3:..... several others

Point groups

Symmetry of molecules are represented by the collection of symmetry operations leaving it unchanged, i.e. by the *point group*.

Point groups are represented by the so called *Schoenflies-symboles*:

- C_n: groups including proper rotation $\hat{C}_n$ only
- C_{nv}: groups including proper rotation $\hat{C}_n$ and reflection to a plain including the axis $\hat{\sigma}_v$
- C_{nh}: groups including proper rotation $\hat{C}_n$ and reflection to a plain perpendicular to the axis $\hat{\sigma}_h$
- D_n: groups including proper rotation $\hat{C}_n$ and n additional proper rotation $\hat{C}_2$ perpendicular to the main axis
- D_{nh}: same as D_n with and additional reflection to a plane perpendicular to the main axis.

Point groups

- D_{nd}: same as D_n with and additional reflection to a plane including the main axis.
- S_n: includes improper rotation $\hat{S}_n$
- T_d: tetrahedral point group
- ...
- $C_{\infty v}$: proper rotation with arbitrary angle ($\hat{C}_\infty$) and reflection to a plane including this axis ($\hat{\sigma}_v$)
- $D_{\infty h}$: proper rotation with arbitrary angle ($\hat{C}_\infty$) and reflection to a plane perpendicular to this axis ($\hat{\sigma}_h$)
- O_3^+: spherical symmetry

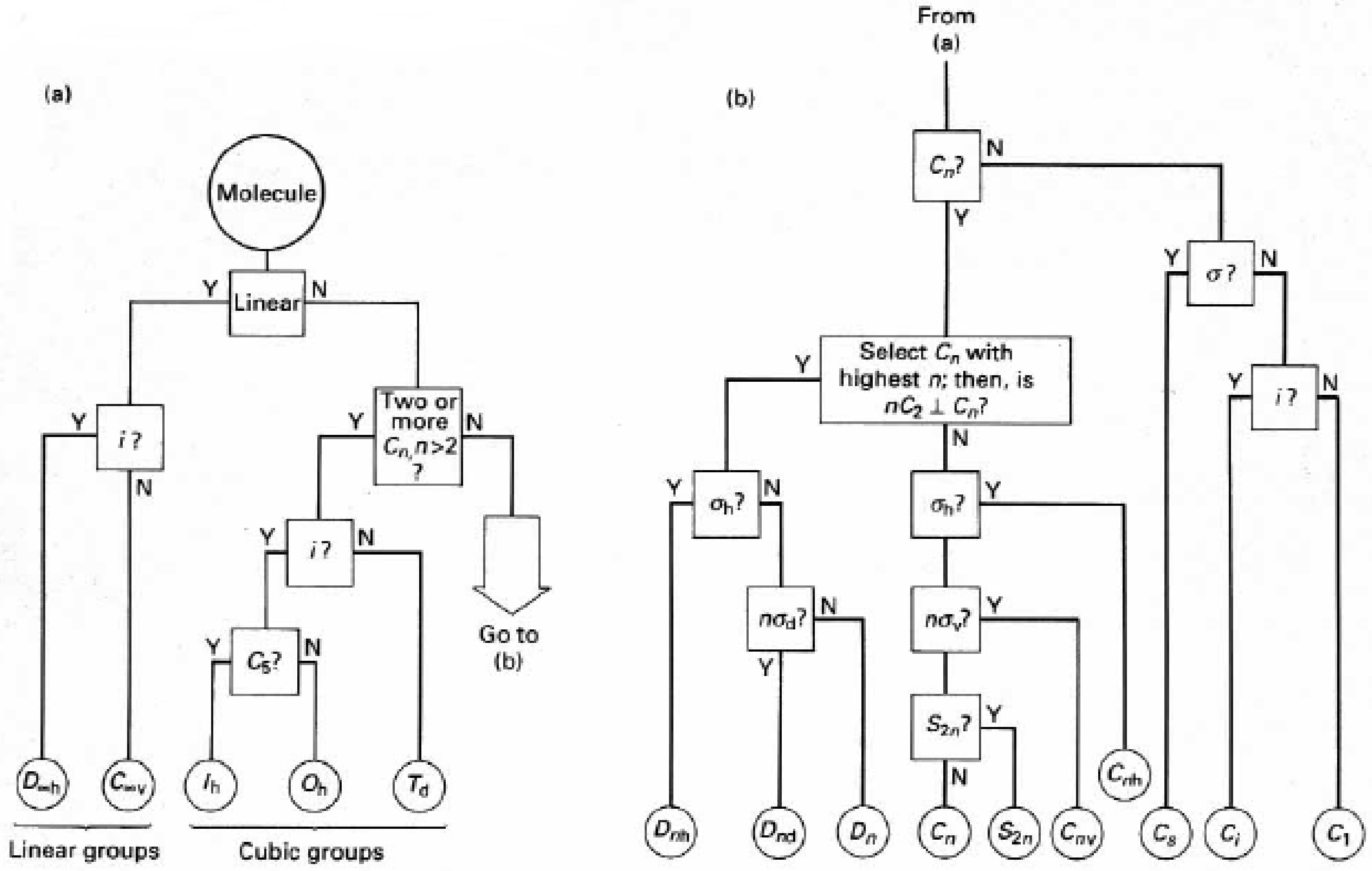
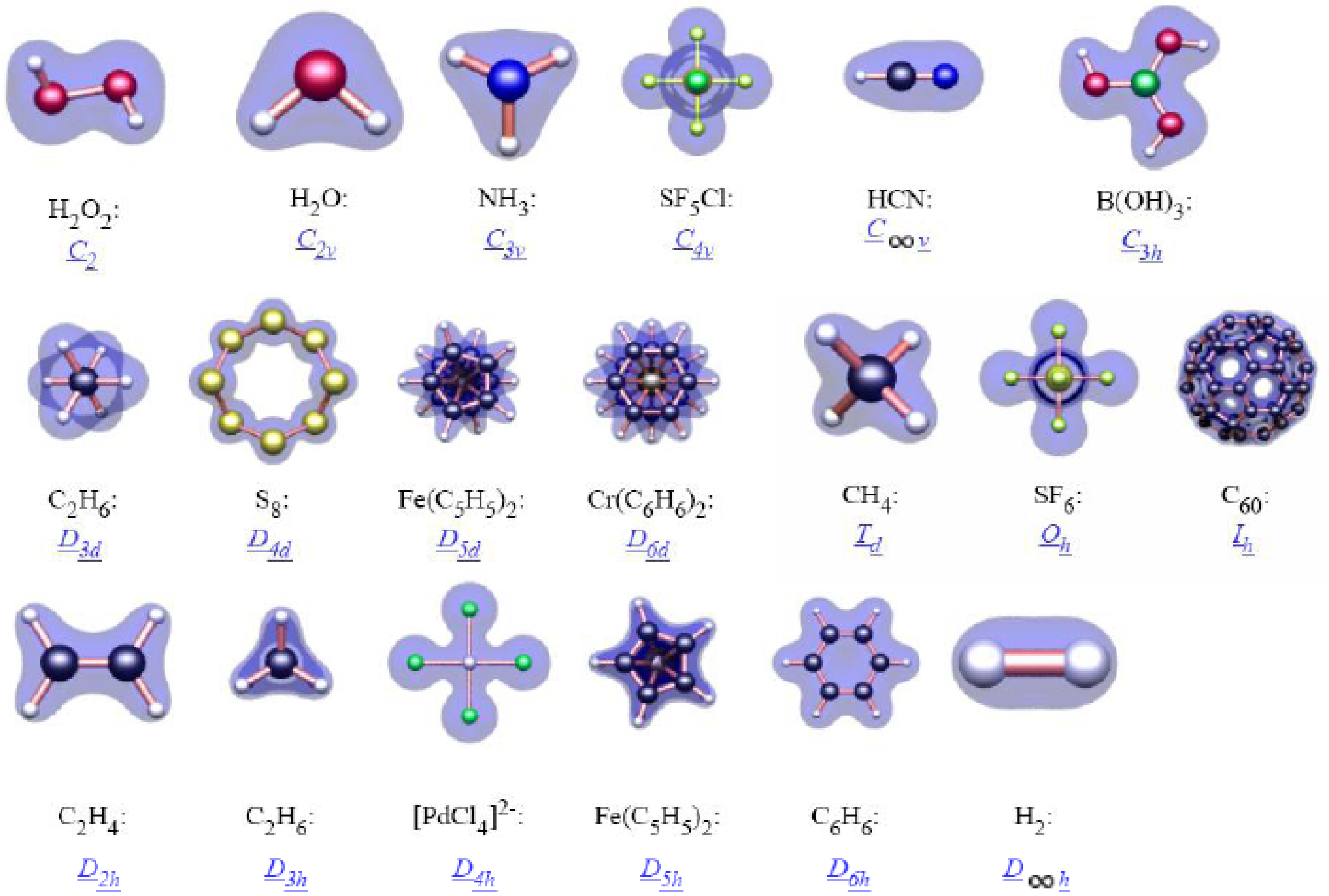


Figure 3.15
Shriver, Atkins, and Langford: *INORGANIC CHEMISTRY*, second edition
©1990, 1994 D. F. Shriver, P. W. Atkins, and C. H. Langford
W. H. Freeman and Company

Point groups

Molecular examples:

molecule	symmetry operations	point group
water	$\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$	C_{2v}
ammonia	$\hat{C}_3(z)$, 3 x $\hat{\sigma}_v$, $\hat{E}$	C_{3v}
benzene	$\hat{C}_6$, 6 x $\hat{C}_2$, $\hat{\sigma}_h$, 6 x $\hat{\sigma}_v$, $\hat{i}$, etc.	D_{6h}
formaldehyde	$\hat{C}_2(z)$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$	C_{2v}
ethene		D_{2h}
acetylene		$D_{\infty h}$
carbon monoxide		$C_{\infty v}$



H_2O_2: C_2

H_2O: C_{2v}

NH_3: C_{3v}

SF_5Cl: C_{4v}

HCN: $C_{\infty v}$

$B(OH)_3$: C_{3h}

C_2H_6: D_{3d}

S_8: D_{4d}

$Fe(C_5H_5)_2$: D_{5d}

$Cr(C_6H_6)_2$: D_{6d}

CH_4: T_d

SF_6: O_h

C_{60}: I_h

C_2H_4: D_{2h}

C_2H_6: D_{3h}

$[PdCl_4]^{2-}$: D_{4h}

$Fe(C_5H_5)_2$: D_{5h}

C_6H_6: D_{6h}

H_2: $D_{\infty h}$

http://newton.ex.ac.uk/research/qsystems/people/goss/symmetry/Molecules.html

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Symmetry and quantum mechanics

Symmetry and quantum mechanics

Symmetry operations are represented by operators ($\hat{R}$).

What does it mean mathematically that the operation leaves the molecule unchanged?

It does not change the properties → The symmetry operators commute with the corresponding operators (e.g. Hamiltonian):

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

Symmetry and quantum mechanics

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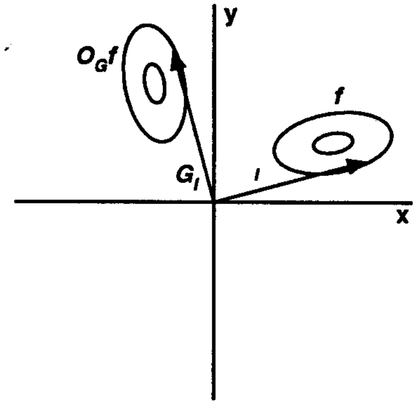
Figure 10.2: Transformation of functions



Action of a symmetry operator on a function:

$$\hat{R}f(\mathbf{x}) = f(\hat{R}^{-1}\mathbf{x})$$

Symmetry and quantum mechanics

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

Commuting operators have a common set of eigenfunctions[2]

$\Downarrow$

The eigenfunction of the Hamiltonian must also be eigenfunction of the symmetry operators.

$$\hat{R}\Psi = r\Psi$$

---

[2] For easier understanding we disregard degeneracy for a while.

Symmetry and quantum mechanics

$$\hat{R}\Psi \quad = \quad r\Psi$$

What are the eigenvalues?

- Like the object (molecule), the wave function is unchanged under the symmetry operation: $r = 1$
- The wave function can also change sign under the symmetry operation, since in this case the density $|\Psi|^2$ is still unchanged: $r = -1$

This eigenvalue will be representative for the wave function ("good quantum numbers"):

- $r = 1$: symmetric
- $r = -1$: antisymmetric

Symmetry and quantum mechanics

$$\hat{R}\Psi \quad = \quad r\Psi$$

What about the eigenfunctions?

- They form a basis for a representation

Symmetry axiom: the eigenfunctions of the Hamiltonian form an *irreducible representation* of the symmetry operations.

Symmetry and quantum mechanics

We have several symmetry operations, all can have two eigenvalues.

For water, this means 2^3 possibilities ($\hat{E}$ has only one eigenvalue).

Are all of these possible?? No, only four combinations are possible:

C_{2v}	E	C_2	σ_{zx}	σ_{zy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

The four possibilities are the *irreducible representation*.

The *character table* shows the eigenvalue of the individual operators corresponding to the irreps.

Thus, wave functions can be classified according to the rows of the character table, i.e. according to the irreps.

Symmetry and quantum mechanics

We have several symmetry operations, all can have two eigenvalues.

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B_2	1	-1	-1	1

The four possibilities are the *irreducible representation*.

The *character table* shows the eigenvalue of the individual operators corresponding to the irreps.

Thus, the wave function of water can be classified as A_1, A_2, B_1 or B_2.

Symmetry and quantum mechanics

Other example: ammonia

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Here there is also two-dimensional irrep. This means:

- there are two eigenfunctions of the Hamiltonian which have the same symmetry property
- any combination of these two functions still define a representation of the group (with the same character)

Symmetry and quantum mechanics

Other example: ammonia

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Here there is also two-dimensional irrep. This means:

- there are two eigenfunctions of the Hamiltonian which have the same symmetry property
- any combination of these two functions still define a representation of the group (with the same character)

⇒ it is logical that these functions belong to the same eigenvalue of the Hamiltonian, i.e. *degenerate*!

Symmetry and quantum mechanics

In summary:

It is worth to use symmetry:

- to classify states
- to speed up calculations

.

Permutation symmetry: Symmetric group

Permutation symmetry: Symmetric group

n objects can be arranged in $n!$ different ways.

Permutation operator:

$$\hat{P} = \begin{pmatrix} 1 & 2 & \cdots & n \\ i_1 & i_2 & \cdots & i_n \end{pmatrix}$$

meaning that 1 is replaced by i_1, 2 by i_2, etc.

Action on a function:

$$\hat{P}F(x_1, x_2, ..., x_n) = F(x_{i_1}, x_{i_2}, ..., x_{i_n})$$

Permutation symmetry: Symmetric group

S_n group: formed by the permutations of n objects

Multiplication defined by:

$$\begin{pmatrix} i_1 & i_2 & \cdots & i_n \\ k_1 & k_2 & \cdots & k_n \end{pmatrix}\begin{pmatrix} 1 & 2 & \cdots & n \\ i_1 & i_2 & \cdots & i_n \end{pmatrix} = \begin{pmatrix} 1 & 2 & \cdots & n \\ k_1 & k_2 & \cdots & k_n \end{pmatrix}$$

Unit element:

$$\hat{P}_E = \begin{pmatrix} 1 & 2 & \cdots & n \\ 1 & 2 & \cdots & n \end{pmatrix}$$

Inverse:

$$\hat{P}^{-1} = \begin{pmatrix} i_1 & i_2 & \cdots & i_n \\ 1 & 2 & \cdots & n \end{pmatrix}$$

Permutation symmetry: Symmetric group

Cyclic permutations:

$$\begin{pmatrix} i_1 & i_2 & \cdots & i_n \\ i_2 & i_3 & \cdots & i_1 \end{pmatrix} = \begin{pmatrix} i_1 & i_2 & \cdots & i_n \end{pmatrix}$$

Each number is replaced by the one standing after the number.

Any arbitrary permutation can be decomposed into the product of independent cycles, e.g.

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 3 & 4 & 5 & 2 & 1 & 7 & 6 \end{pmatrix} = \begin{pmatrix} 1 & 3 & 5 \end{pmatrix}\begin{pmatrix} 2 & 4 \end{pmatrix}\begin{pmatrix} 6 & 7 \end{pmatrix}$$

Cyclyc structure: The above permutation has a cyclic structure of $3\ 2^2$, i.e. it is composed of a 3 and two 2 element cycles.

Permutation symmetry: Symmetric group

Transposition: cycle of order 2

An arbitrary permutation can be decomposed as a product of transpositions:

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 3 & 4 & 5 & 2 & 1 & 7 & 6 \end{pmatrix} = \begin{pmatrix} 1 & 3 \end{pmatrix}\begin{pmatrix} 3 & 5 \end{pmatrix}\begin{pmatrix} 2 & 4 \end{pmatrix}\begin{pmatrix} 6 & 7 \end{pmatrix}$$

it was used that

$$\begin{pmatrix} 1 & 3 & 5 \end{pmatrix} = \begin{pmatrix} 1 & 3 \end{pmatrix}\begin{pmatrix} 3 & 5 \end{pmatrix}$$

Permutation symmetry: Symmetric group

Conjugate elements:

$\hat{T}_1$ and $\hat{T}_2$ are conjugate, if there exists an $\hat{S}$ in the group that:

$$\hat{T}_1 \quad = \quad \hat{S}\,\hat{T}_2\,\hat{S}^{-1}$$

- Conjugate elements form classes
- Conjugate elements have the same cyclic structure.

Therefore,

- classes can be characterized by their cyclic structure
- the number of classes of the symmetric group is given by the number of possible cyclic structures.

Permutation symmetry: Symmetric group

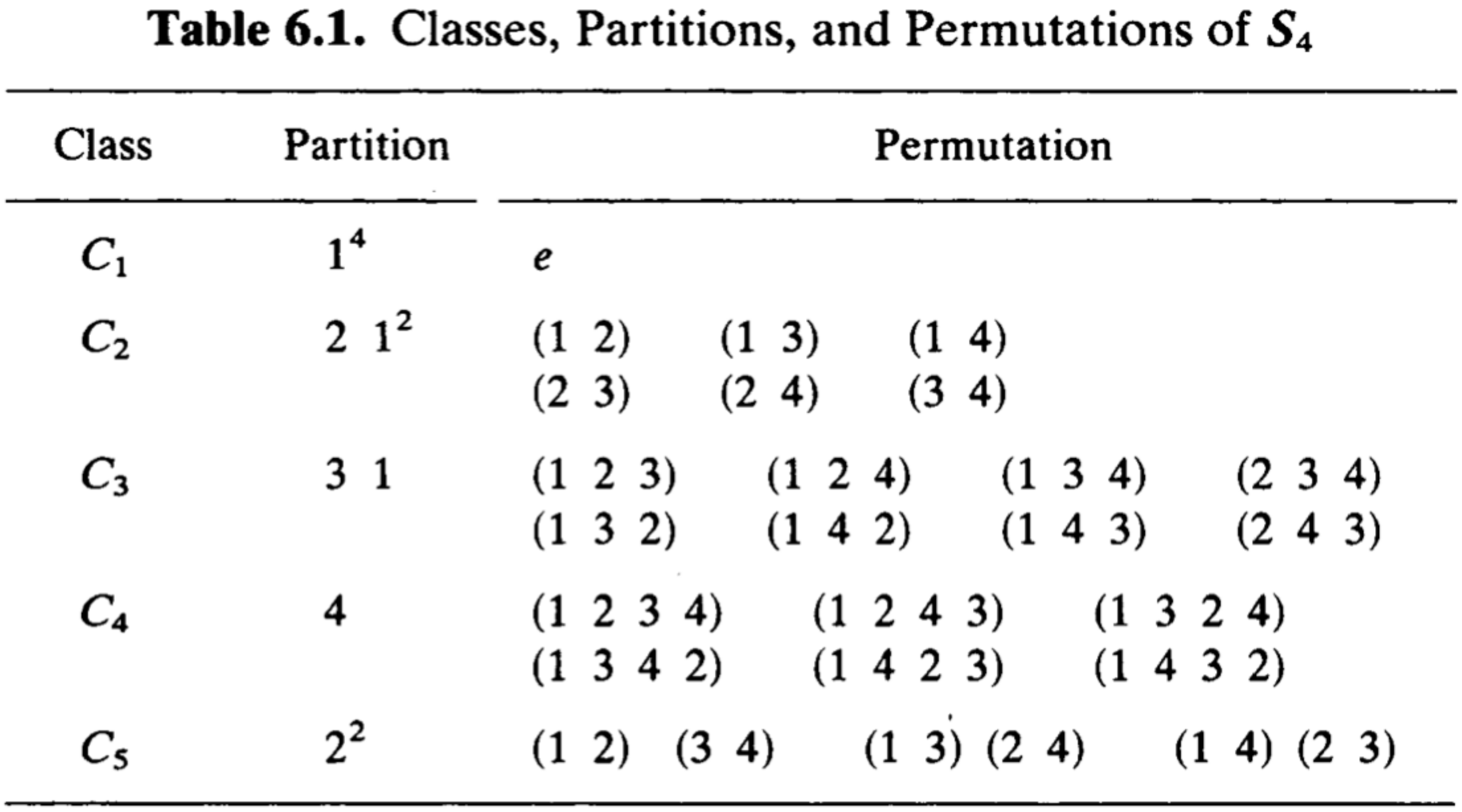


Table 6.1. Classes, Partitions, and Permutations of S_4

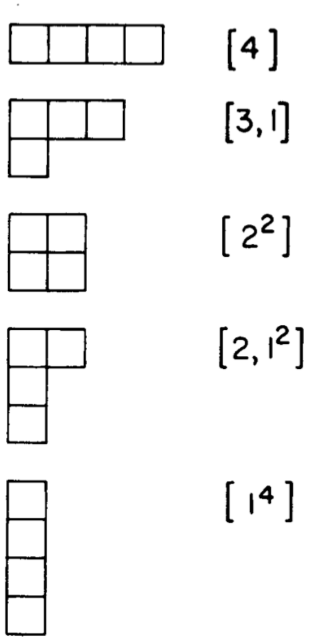
Class	Partition	Permutation			
C_1	1^4	e			
C_2	$2\ 1^2$	(1 2)	(1 3)	(1 4)	
		(2 3)	(2 4)	(3 4)	
C_3	3 1	(1 2 3)	(1 2 4)	(1 3 4)	(2 3 4)
		(1 3 2)	(1 4 2)	(1 4 3)	(2 4 3)
C_4	4	(1 2 3 4)	(1 2 4 3)	(1 3 2 4)	
		(1 3 4 2)	(1 4 2 3)	(1 4 3 2)	
C_5	2^2	(1 2) (3 4)	(1 3) (2 4)	(1 4) (2 3)	

Permutation symmetry: Symmetric group

Young frames: visualizations of different partitions

For a partition $\lambda_1, \lambda_2, \lambda_3, ..., \lambda_n$ (increasing order) the Young frame is a diagram with λ_1 boxes in the first row, λ_2 boxes in the second row, etc.

For the previous example:



Permutation symmetry: Symmetric group

Young tableau:

- Young frame filled up with numbers 1 to n ($n!$ possibilities).

$[4]$:

1	2	3	4

1	2	4	3

1	3	2	4

1	3	4	2

1	4	2	3

1	4	3	2

$[3, 1]$:

1	2	3
4		

1	2	4
3		

1	3	4
2		

2	3	4
1		

1	3	2
4		

1	4	2
3		

1	4	3
2		

2	4	3
1		

Permutation symmetry: Symmetric group

Standard tableau:

- Those Young tableaux where the elements increase in each row from left to right and in each column from top to bottom.

Permutation symmetry: Symmetric group

Standard tableau:

- Those Young tableaux where the elements increase in each row from left to right and in each column from top to bottom.

$[4]$:

$$\begin{array}{|c|c|c|c|}\hline 1 & 2 & 3 & 4 \\ \hline \end{array}$$

$[3,1]$:

$$\begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline \multicolumn{1}{|c|}{4} \\ \cline{1-1} \end{array} \qquad \begin{array}{|c|c|c|}\hline 1 & 2 & 4 \\ \hline \multicolumn{1}{|c|}{3} \\ \cline{1-1} \end{array} \qquad \begin{array}{|c|c|c|}\hline 1 & 3 & 4 \\ \hline \multicolumn{1}{|c|}{2} \\ \cline{1-1} \end{array}$$

There are simple rules to calculate the number of standard tableaux (see Paunz).

Generators of the symmetric group

The generators of the symmetric group are the *basic transpositions:*

$$\hat{\sigma}_i \;=\; \left(\; i \quad i+1 \;\right)$$

i.e. n-1 generators: (1 2), (2 3), ... (n-1 n).

We have seen that a permutation can be obtained as product of transpositions. Now we have to show that any transposition can be given as products of *basic transpositions*.

Demonstration:

$$\left(\; 1 \quad 3 \;\right) 1\,2\,3 \;=\; 3\,2\,1$$

$$\begin{aligned}
\left(\; 1 \quad 2 \;\right)\left(\; 2 \quad 3 \;\right)\left(\; 1 \quad 2 \;\right) 1\,2\,3 &= \left(\; 1 \quad 2 \;\right)\left(\; 2 \quad 3 \;\right) 2\,1\,3 \\
&= \left(\; 1 \quad 2 \;\right) 2\,3\,1 \\
&= 3\,2\,1
\end{aligned}$$

Representations of the symmetric group

The number of classes equals the number of partitions, i.e. the number of Young shapes.

The number of irreducible representations equals the number classes
→ the symmetric group has as many irreps as Young shapes are there.

According to Young theory:

- the irreps of the symmetric group are also characterized by Young shapes;
- the dimension of the irreps is given by the number of *standard tableaux*;
- the irreps are generated by the subgroup chain: $S_n \supset S_{n-1} \supset \ldots \supset S_2$;
- the standard tableaux can be used calculate the matrix elements of the basic transposition (k-1, k)
  → all matrices can be obtained by matrix multiplication.

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Unitary Group

Unitary Group

Unitary matrices:

$$\mathbf{U}^\dagger \quad = \quad \mathbf{U}^{-1}$$

Unitary matrices form a group:

- product of unitary matrices are unitary matrices
- unit matrix is unitary → unit element
- inverse of unitary matrix (the adjoint) is unitary → inverse element

This group is called *unitary group* $U(n)$.

Unitary Group

Parametrization of unitary matrices:

$$\mathbf{U} = \exp(i\mathbf{A})$$

with $\mathbf{A}$ being a Hermitian matrix, which can be written as:

$$\mathbf{A} = \sum_{i,j=1} \alpha_{ij}\mathbf{e_{ij}}$$

with $\alpha_{ij} = \alpha^*_{ij}$.

$\mathbf{e_{ij}}$: *basic matrix unit*, with all elements 0, except $\{i,j\}$, which is one.

Properties:

$$[\mathbf{e_{ij}}, \mathbf{e_{kl}}] = \delta_{jk}\mathbf{e_{il}} - \delta_{li}\mathbf{e_{kj}}$$

Unitary Group

Generators of the unitary group

$\mathbf{e_{ij}}$ is practically the generator of $\mathbf{A}$. But we need a generator for the unitary matrices $\mathbf{U}$.

One-parameter subgroup:

$$\mathbf{U}(t) \quad = \quad \exp(it\mathbf{H})$$

where $\mathbf{H}$ is a fixed matrix, and t is varied continuously.

- multiplication: $\mathbf{U}(t)\mathbf{U}(t') = \mathbf{U}(t + t')$
- unit element: $\mathbf{U}(0) = \mathbf{E}$
- inverse: $\mathbf{U}(t)^{-1} = \mathbf{U}(-t)$

Unitary Group

Generators of the unitary group

Now we can define a basic set of one-parameter subgroups with the *basic matrix units* as $\mathbf{H}$:

$$\begin{aligned}
\mathbf{U_{kk}}(t) &= \exp(it\mathbf{e_{kk}}) \\
\mathbf{U_{kl}}(t) &= \exp[it(\mathbf{e_{kl}}+\mathbf{e_{lk}})/2] \qquad k<l \\
\mathbf{U_{lk}}(t) &= \exp[it(\mathbf{e_{kl}}-\mathbf{e_{lk}})/2i] \qquad k>l
\end{aligned}$$

These matrices can be considered as a *basis* since an arbitrary unitary matrix can be given as a product of these matrices.

Note that the size of this basis sets is n^2.

Unitary Group

Generators of the unitary group

Now we need the generators independent of t. These can be given as:

$$\begin{aligned}
\hat{E}_{rr} &= -i\hat{X}_{rr} \\
\hat{E}_{rs} &= -i\hat{X}_{rs} + \hat{X}_{sr} \quad r < s \quad \text{raising generator} \\
\hat{E}_{sr} &= -i\hat{X}_{rs} - \hat{X}_{sr} \quad r < s \quad \text{lowering generator}
\end{aligned}$$

with

$$\hat{X}_{kl} = \left[\frac{d\hat{O}_{kl}}{dt}\right]_{t=0}$$

where $\hat{O}_{kl}$ is an operator corresponding to the unitary matrix $\mathbf{U_{kl}}$.

Unitary Group

Generators of the unitary group

Now we need the generators independent of t. These can be given as:

$$\begin{aligned}
\hat{E}_{rr} &= -i\hat{X}_{rr} && \\
\hat{E}_{rs} &= -i\hat{X}_{rs} + \hat{X}_{sr} \quad r < s && \text{raising generator} \\
\hat{E}_{sr} &= -i\hat{X}_{rs} - \hat{X}_{sr} \quad r < s && \text{lowering generator}
\end{aligned}$$

with

$$\hat{X}_{kl} = \left[\frac{d\hat{O}_{kl}}{dt}\right]_{t=0}$$

where $\hat{O}_{kl}$ is an operator corresponding to the unitary matrix $\mathbf{U_{kl}}$.

$\{\hat{E}_{rs}\}$ are the *generators* (or *infinitesimal operators*) of the representation.

Unitary Group

Generators of the unitary group

Important property of the generators of the unitary group:

$$[\hat{E}_{rs}, \hat{E}_{tu}] \quad = \quad \delta_{st}\hat{E}_{ru} - \delta_{ru}\hat{E}_{ts}$$

Note that these commutation relations are the same as that of the basic excitation operators used to define the second quantized Hamiltonian.

Unitary Group

Irreducible representations of the unitary group

Gel'fand and Tsetlin introduced a way to label the vectors spanning the space of the irreducible representation. It is based on hierarchical procedure using the sequence of subgroups:

$$U(n) \supset U(n-1) \supset ... \supset U(2) \supset U(1)$$

The vectors are given by the following symbol (*Gel'fand pattern*):

$$(m)_n = \begin{array}{ccccccc} m_{1n} & & m_{2n} & \cdots & & & m_{nn} \\ & m_{1,n-1} & & \cdots & & m_{n-1,n-1} & \\ & & m_{12} & & m_{22} & & \\ & & & m_{11} & & & \end{array}$$

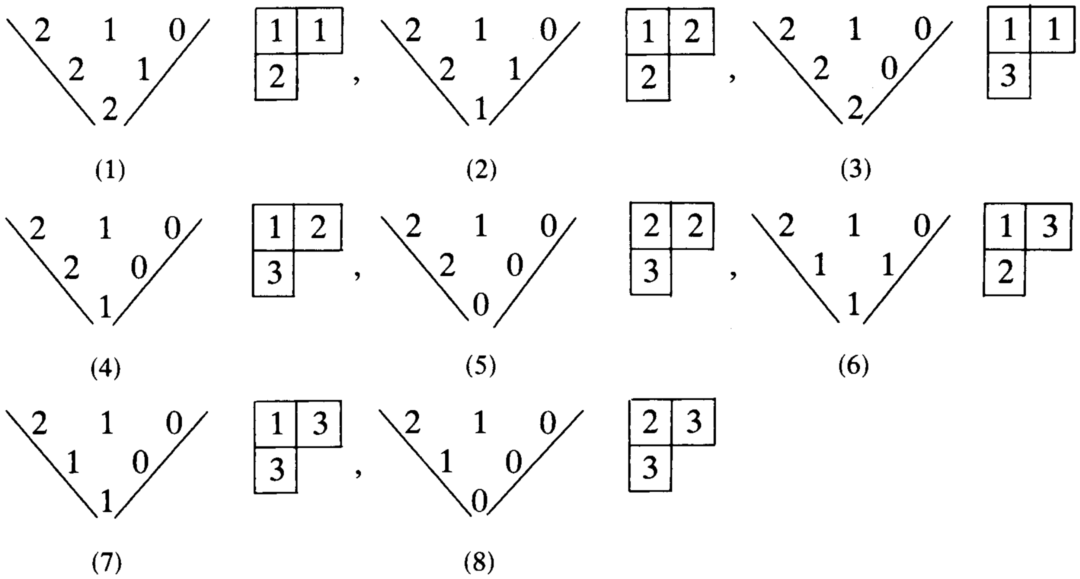
What is important that the matrix elements of the generators $\hat{E}_{rs}$ could be given by Gel'fand and Tsetlin using the parameters labeling these vectors.

Unitary Group

Weyl tableau

This is an alternative reresentation of the Gel'fand-Tsetlin basis, in particular useful for electronic structure calculations. It resembles the Young tableau, but the meaning of the boxes and their content is different.

Refraining again from going into details, here is an example of this relationship:

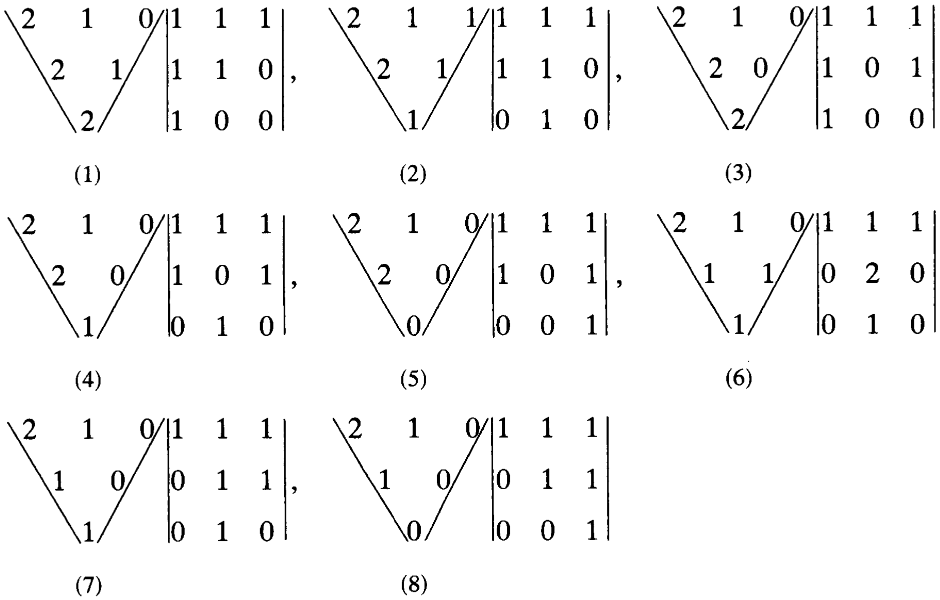


Unitary Group

Paldus tableau

This is an alternative reresentation of the Gel'fand-Tsetlin basis, in particular useful for electronic structure calculations.

Refraining again from going into details, here is an example of this relationship:



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Construction of spin functions

Construction of spin functions

z component of the spin:

$$\hat{S}_z = \sum_{l=1}^{N} \hat{s}_z(l)$$

i.e. sum of one-electron components, so that its eigenfunctions are products:

$$\Theta_i = \theta(1)\theta(2)...\theta(N)$$

with $\theta(l)$ being α or β.

The 2^N-dimensional subspace can be decomposed according to the eigenvalues of $\hat{S}_z$:

$$\hat{S}_z\Theta_l(\mu,\nu) = \frac{1}{2}(\mu-\nu)\Theta_i(\mu,\nu)$$

$\Theta_i(\mu,\nu)$ is the *primitive spin function* with μ α functions and ν β functions.

Construction of spin functions

$\hat{S}^2$ is not a sum of individual components, so eigenfunctions can not be given as product of the individual components.

Two useful expressions of the $\hat{S}^2$ operator:

$$\hat{S}^2 = \frac{-N(N-4)}{4} + \sum_{i<j} \hat{P}_{ij} \tag{1}$$

with $\hat{P}_{ij}$ being the permutation operator of electrons i and j.

$$\hat{S}^2 = \hat{S}_+\hat{S}_- + \hat{S}_z^2 - \hat{S}_z \tag{2}$$

with $\hat{S}_+$ and $\hat{S}_-$ as step-up and step-dow spin operators, respectively.

Construction of spin functions

There are several methods for constructing $\hat{S}^2$ eigenfunctions:

1. Diagonalization
   One can use the fact that: $[\hat{S}^2, \hat{S}_z] = 0$

   i.e. $\hat{S}^2$ and $\hat{S}_z$ have common eigenvectors.

2. Genealogical construction
   Stepwise construction by adding one more spin function at a time

3. Using projection operators

4. Using spin pair functions

5. ....

Construction of spin functions

Method 1: diagonalization in the subspace corresponding to the $M = \frac{1}{2}(\mu - \nu)$ eigenvalues of $\hat{S}_z$.

Example: $N = 3, M = \frac{1}{2}$

$$\Theta_1 = \alpha\alpha\beta \qquad \Theta_2 = \alpha\beta\alpha \qquad \Theta_3 = \beta\alpha\alpha$$

$$\mathbf{S^2} \quad = \quad \begin{pmatrix} 1\frac{3}{4} & 1 & 1 \\ 1 & 1\frac{3}{4} & 1 \\ 1 & 1 & 1\frac{3}{4} \end{pmatrix}$$

Eigenvectors:

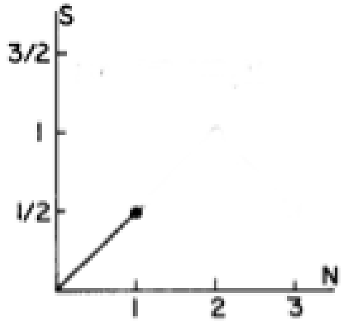
$$\begin{aligned} X_1 &= 3^{-1/2}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha) \qquad S = \frac{3}{2} \\ X_2 &= 6^{-1/2}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) \qquad S = \frac{1}{2} \\ X_1 &= 2^{-1/2}(\alpha\beta\alpha - \beta\alpha\alpha) \qquad S = \frac{1}{2} \end{aligned}$$

This is a straightforward procedure but can be tedious for lots of electrons.

Construction of spin functions

Method 2: Genealogical construction of spin eigenfunctions

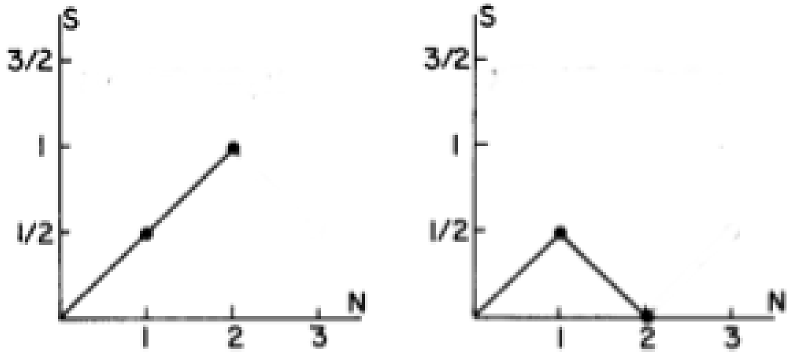
Possible eigenstates:



- Single electron:

  $S = \frac{1}{2}$ with $M = \frac{1}{2}$ or $M = -\frac{1}{2}$

- Two electron case:
  - $S = 1$ triplet state by increasing the spin of single electron case
  - $S = 0$ singlet state by decreasing the spin of single electron case



Construction of spin functions

Method 2: Genealogical construction of spin eigenfunctions

Possible eigenstates:

- Three electron case:

  We can get $S = \frac{1}{2}$ states from both two electron cases:

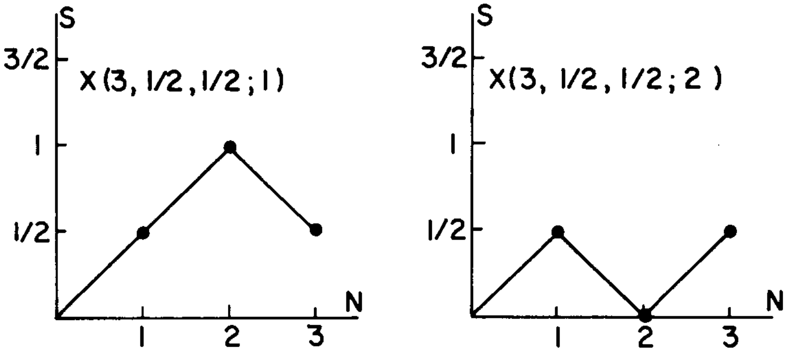


Figure 2.1. Branching-diagram functions for $N = 3$, $S = \frac{1}{2}$.

Construction of spin functions

Method 2: Genealogical construction of spin eigenfunctions

How can we construct the eigenfunctions along the branching diagram?

First a notation:

$$X(N, S, M; l)$$

denotes the lth eigenfunction of the N electron spin function with S and M quantum numbers.

Single electron:

$$\begin{aligned} X\left(1, \frac{1}{2}, \frac{1}{2}; 1\right) &= \alpha \\ X\left(1, \frac{1}{2}, -\frac{1}{2}; 1\right) &= \beta \end{aligned}$$

Construction of spin functions

Method 2: Genealogical construction of spin eigenfunctions

How can we construct the eigenfunctions along the branching

Recursive formula for constructing N electron eigenfunction from $N-1$ eigenfunction:

- Addition, i.e. S from $S-\frac{1}{2}$ function:

$$\begin{aligned} X(N,S,M;l) \quad &= \quad \frac{1}{\sqrt{2S}}\Big[(S+M)^{\frac{1}{2}}\ X(N-1,S-\frac{1}{2},M-\frac{1}{2};k)\ \alpha(N) \\ &\qquad +(S-M)^{\frac{1}{2}}\ X(N-1,S-\frac{1}{2},M+\frac{1}{2};k)\ \beta(N)\Big] \end{aligned}$$

- Substruction, i.e. S from $S+\frac{1}{2}$ function:

$$\begin{aligned} X(N,S,M;l) \quad &= \quad \frac{1}{\sqrt{2S+2}}\Big[-(S-M+1)^{\frac{1}{2}}\ X(N-1,S+\frac{1}{2},M-\frac{1}{2};k)\ \alpha(N) \\ &\qquad +(S+M+1)^{\frac{1}{2}}\ X(N-1,S+\frac{1}{2},M+\frac{1}{2};k)\ \beta(N)\Big] \end{aligned}$$

Construction of spin functions

Branching diagram:

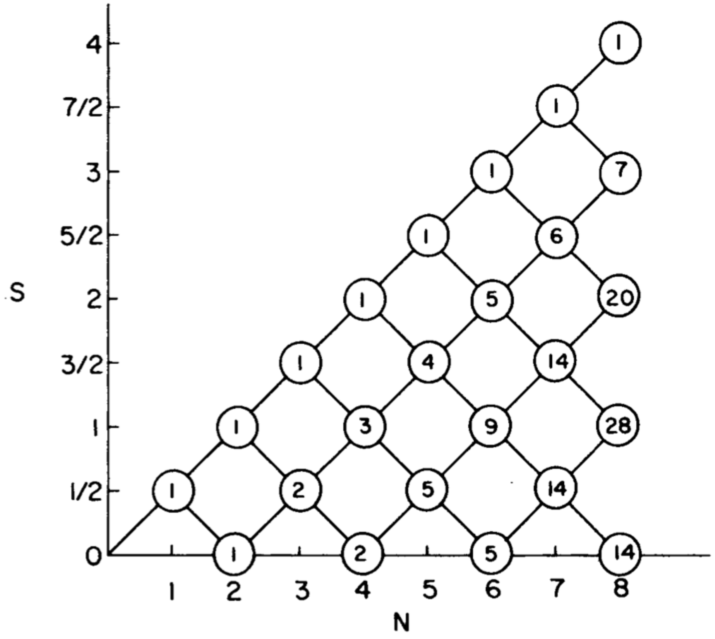


Figure 2.2. Branching diagram.

- vertices specify the values N and S
- spin functions can be created along the graph leading to the desired N and S value
- number in the circles indicate the number of independent spin states

$$f(N,S) = f(N-1,S+1/2) + f(N-1,S-1/2) = \begin{pmatrix} N \\ \frac{1}{2}N - S \end{pmatrix} - \begin{pmatrix} N \\ \frac{1}{2}N - S - 1 \end{pmatrix}$$

Symmetric group and spin

Permutation commute with spin operators since these are symmetric in electronic coordinates:

$$[\hat{P}, \hat{S}_z] = 0 \qquad [\hat{P}, \hat{S}^2] = 0$$

Therefore spin eigenfunctions ($X(N, S, M; k)$) belonging to the same eigenvalues form a basis for representation of $\hat{P}$:

$$\hat{P}X(N, S, M; k) \;\; = \;\; \sum_l X(N, S, M; l) P_{lk}$$

with

$$P_{lk} \;\; = \;\; \langle X(N, S, M; l) | \hat{P} | X(N, S, M; k) \rangle$$

Spin functions form an irreducible representation of the symmetric group!

Symmetric group and spin

There is one-to-one correspondance between branching-diagram functions and standard Young tableau:

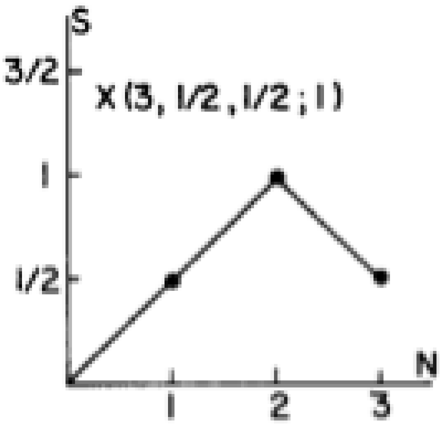
- the space is spanned by functions of a given $M = \mu - \nu$, i.e. the μ α and ν β functions are there.
- this corresponds to a partition μ ν $\Rightarrow$ Young tableau includes μ boxes in the first row and ν boxes in the second row.
- for branching-diagram functions a standard Young tableaux should be created.

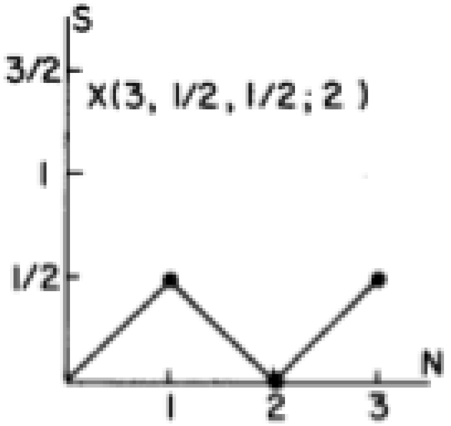
Moreover, one can show that the matrix elements are the same as the ones obtained with Young orthogonal representation → group theoretical methods can be used to calculate the spin-related matrix elements.

Symmetric group and spin

There is one-to-one correspondence between branching-diagram functions and standard Young tableau:

Example for the correspondence: $N = 3$, $S = \frac{1}{2}$



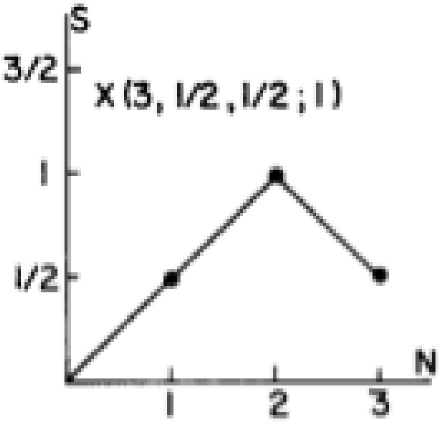


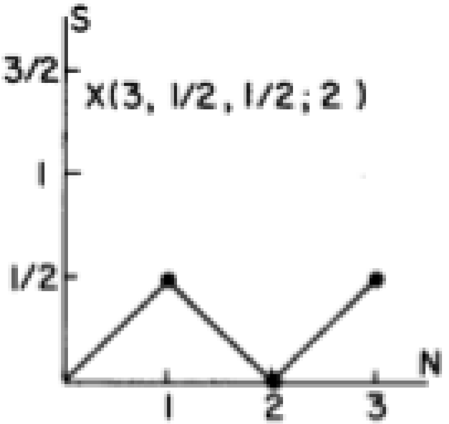
$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array} \qquad \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1}\end{array}$$

Symmetric group and spin

There is one-to-one correspondence between branching-diagram functions and standard Young tableau:

Example for the correspondence: $N = 3$, $S = \frac{1}{2}$





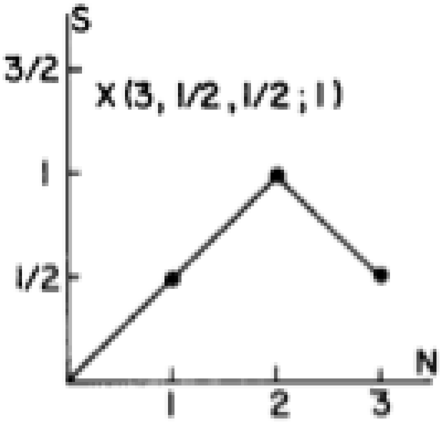
$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array} \qquad \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1}\end{array}$$

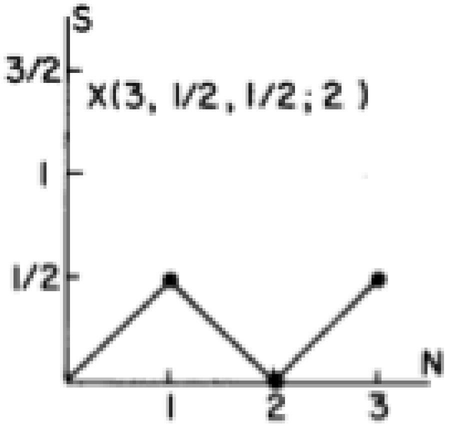
$\neq \alpha(1)\alpha(2)\beta(3)$ $\neq \alpha(1)\beta(2)\alpha(3)$

Symmetric group and spin

There is one-to-one correspondence between branching-diagram functions and standard Young tableau:

Example for the correspondence: $N = 3$, $S = \frac{1}{2}$





$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array} \qquad \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

$=\alpha(1)\alpha(2)\beta(3)-\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3)$ $=\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3)$

Symmetric group and spin

N	S	M	spin function	standard Young tabl
1	1/2	1/2	$\alpha(1)$	$\boxed{1}$
1	1/2	-1/2	$\beta(1)$	X
2	1	1	$\alpha(1)\alpha(2)$	$\boxed{1}\boxed{2}$
2	1	-1	$\beta(1)\beta(2)$	X
2	1	0	$\beta(1)\alpha(2)+\alpha(1)\beta(2)$	X
2	0	0	$-\beta(1)\alpha(2)+\alpha(1)\beta(2)$	$\boxed{1}$ $\boxed{2}$
3	3/2	3/2	$\alpha(1)\alpha(2)\alpha(3)$	$\boxed{1}\boxed{2}\boxed{3}$
3	1/2	1/2	$\alpha(1)\alpha(2)\beta(3)-\alpha(1)\beta(2)\alpha(3)-\beta(1)\alpha(2)\alpha(3)$	$\boxed{1}\boxed{2}$ $\boxed{3}$
3	1/2	1/2	$-\beta(1)\alpha(2)\alpha(3)+\alpha(1)\beta(2)\alpha(3)$	$\boxed{1}\boxed{3}$ $\boxed{2}$

Addition: $X(N,S,M;l)=\frac{1}{\sqrt{2S}}\left[(S+M)^{\frac{1}{2}}X\left(N-1,S-\frac{1}{2},M-\frac{1}{2};k\right)\alpha(N)+(S-M)^{\frac{1}{2}}X\left(N-1,S-\frac{1}{2},M+\frac{1}{2};k\right)\beta(N)\right]$

Substruction: $X(N,S,M;l)=\frac{1}{\sqrt{2S+2}}\Big[-(S-M+1)^{\frac{1}{2}}X\left(N-1,S+\frac{1}{2},M-\frac{1}{2};k\right)\alpha(N)$

$+(S+M+1)^{\frac{1}{2}}X\left(N-1,S+\frac{1}{2},M+\frac{1}{2};k\right)\beta(N)\Big]$

Symmetric group and spin

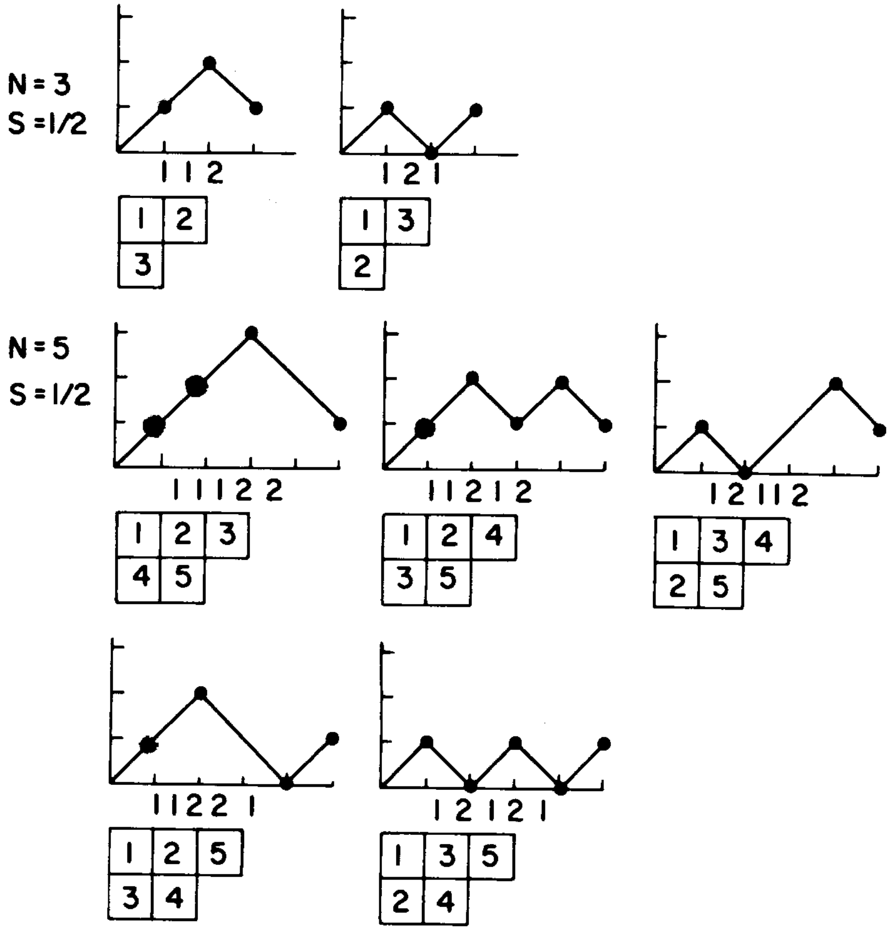


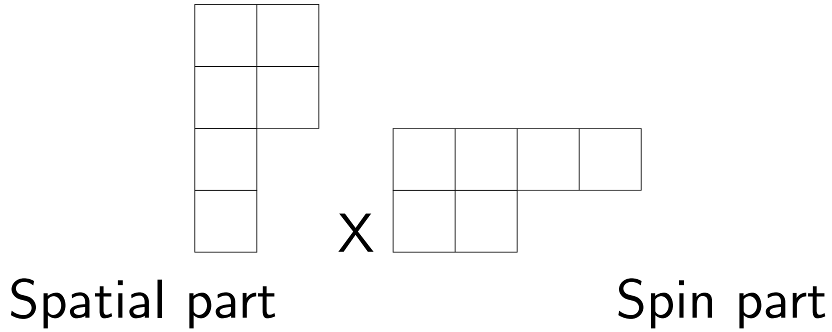
Figure 7.3. Diagrams, branching-diagram symbols, and Young tableaux for $N = 3$, $S = \frac{1}{2}$ and $N = 5$, $S = \frac{1}{2}$.

Spatial part of the wave function

To fullfil global anti-symmetry, not all spatial functions can be paired with a given spin function:

$$\Phi(r; N, S, l')X(N, S, M; l)$$

One can show, that such wave function can be represented by the so called *dual shapes*:



Spin can be integrated out and we are left with:

$$\langle\Phi(r; N, S, l)|\hat{H}|\Phi(r; N, S, m)\rangle$$

Occupation graph and branching diagram

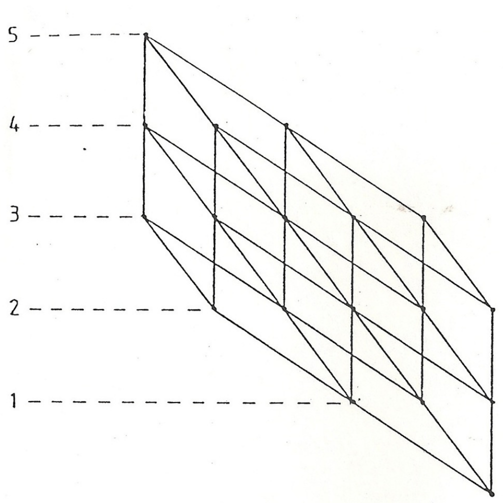


Fig.1 Occupation graph with 5 electrons in 5 orbitals

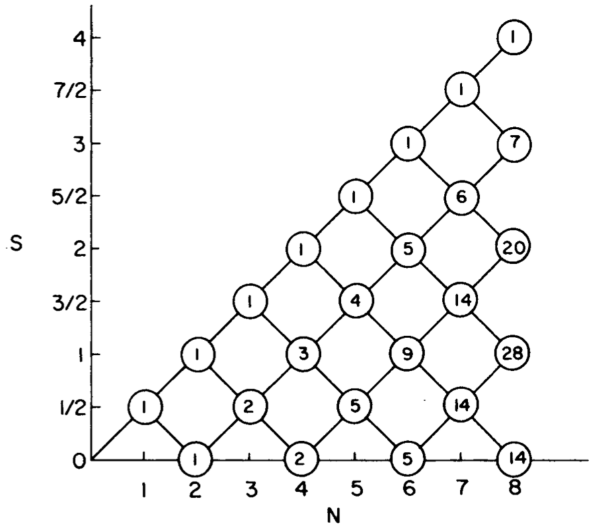


Figure 2.2. Branching diagram.

Representation of CSF's as Gel'fand-Tsetlin basis

Remember the second quantized form of the Hamiltonian:

$$\hat{H} \quad = \quad \sum_{rs} h_{rs}\hat{E}_{rs} + \frac{1}{2}\sum_{rstu}\langle rt|su\rangle[\hat{E}_{rs}\hat{E}_{tu} - \delta_{st}\hat{E}_{ru}]$$

The basic operators $\hat{E}_{rs}$ commute with the spin operators:

$$\left[\hat{S}^2, \hat{E}_{rs}\right] = 0$$

i.e. to construct spin-adapted wave function, the space spanned by the eigenfunctions of $\hat{E}_{rs}$ should be sufficient.

It was also shown that $\hat{E}_{rs}$ is a generator of the unitary group, thus to find the space we can follow the theory of unitary group and construct the corresponding Gel'fand-Tsetlin basis.

Representation of CSF's as Gel'fand-Tsetlin basis

The carrier space for the representation could be the determinants, and we should find the appropriate combinations.

The representative quantities for the functions are the following:

- number of electrons N;
- spin quantum number S;
- number of orbitals n;
- number of paired electrons a;
- number of unpaired electrons b;
- number of empty orbitals c.

The first three are *global* variables, they specify the system and the state we are looking for, therefore equal for all functions (CSFs).

The following relationships must be satisfied:

$$2a + b = N \qquad b = 2S \qquad a + b + c = n$$

Representation of CSF's as Gel'fand-Tsetlin basis

Similarly to the generation of spin-eigenfunctions, we have to distribute N electrons. Still, the procedure is different:

Young tableau	Weyl tableau
μ box for α electrons	a rows with double boxes (paired electrons)
ν box for β electrons	b rows with single box (unpaired electrons)
$\mu + \nu = N$	$2a + b = N$
$\mu - \nu = 2S$	$b = 2S$
$\begin{array}{\|c\|c\|c\|}\hline 1 & 3 & 4 \\ \hline 2 & 5 \\ \cline{1-2} \end{array}$ numbers refer to electrons	$\begin{array}{\|c\|c\|}\hline 1 & 1 \\ \hline 2 & 3 \\ \hline 3 \\ \cline{1-1} \end{array}$ numbers refer to orbitals

Representation of CSF's as Gel'fand-Tsetlin basis

Gel'fand-Tsetlin basis is built up hierarchically:

$$U(n) \supset U(n-1) \supset ... \supset U(2) \supset U(1)$$

i.e. we add orbitals (and electrons) one by one.

We will use the Paldus tableu representation which uses the three numbers a, b, c defined above, and also will draw the Weyl tableau.

The procedure starts from the vacuum: $N = 0$, $S = 0$, $n = 0$:

$$\left| \; a_0 = 0 \quad b_0 = 0 \quad c_0 = 0 \; \right|$$

Representation of CSF's as Gel'fand-Tsetlin basis

$$\left|\ a_0 = 0 \quad b_0 = 0 \quad c_0 = 0\ \right|$$

We add one orbital and one electron, $N = 1$, $S = 1/2$, $n = 1$. In this case the only possibility for the values:

$$\left|\begin{array}{lll} a_1 = 0 & b_1 = 1 & c_1 = 0 \\ a_0 = 0 & b_0 = 0 & c_0 = 0 \end{array}\right| \boxed{1}$$

Representation of CSF's as Gel'fand-Tsetlin basis

$$\left| \begin{matrix} a_0 = 0 & b_0 = 0 & c_0 = 0 \end{matrix} \right|$$

We add one orbital and one electron, $N = 1$, $S = 1/2$, $n = 1$. In this case the only possibility for the values:

$$\left| \begin{matrix} a_1 = 0 & b_1 = 1 & c_1 = 0 \\ a_0 = 0 & b_0 = 0 & c_0 = 0 \end{matrix} \right| \boxed{1}$$

We also could have added two electrons to this orbital, $N = 2$, $S = 0$, $n = 1$.

$$\left| \begin{matrix} a_1 = 1 & b_1 = 0 & c_1 = 0 \\ a_0 = 0 & b_0 = 0 & c_0 = 0 \end{matrix} \right| \quad \boxed{1}\boxed{1}$$

We see that already here we have branching of different constructions.

Representation of CSF's as Gel'fand-Tsetlin basis

Continue from the second one and add one more orbital (n=2). Now we can add zero, one or two electrons.

Representation of CSF's as Gel'fand-Tsetlin basis

Continue from the second one and add one more orbital (n=2). Now we can add zero, one or two electrons.

In the first case nothing changes.

Adding two electrons ($N = 4$), we get:

$$\left| \begin{matrix} a_2 = 2 & b_2 = 0 & c_2 = 0 \\ a_1 = 1 & b_1 = 0 & c_1 = 0 \\ a_0 = 0 & b_0 = 0 & c_0 = 0 \end{matrix} \right| \begin{array}{|c|c|} \hline 1 & 1 \\ \hline 2 & 2 \\ \hline \end{array}$$

which means $S = 0$.

Representation of CSF's as Gel'fand-Tsetlin basis

Continue from the second one and add one more orbital (n=2). Now we can add zero, one or two electrons.

In the first case nothing changes.

Adding two electrons ($N = 4$), we get:

$$\left|\begin{array}{ccc} a_2 = 2 & b_2 = 0 & c_2 = 0 \\ a_1 = 1 & b_1 = 0 & c_1 = 0 \\ a_0 = 0 & b_0 = 0 & c_0 = 0 \end{array}\right| \begin{array}{|c|c|}\hline 1 & 1 \\ \hline 2 & 2 \\ \hline \end{array}$$

which means $S = 0$.

Adding instead one electron ($N = 3$) which implies also $S = 1/2$, that is the spin increased:

$$\left|\begin{array}{ccc} a_2 = 1 & b_2 = 1 & c_2 = 0 \\ a_1 = 1 & b_1 = 0 & c_1 = 0 \\ a_0 = 0 & b_0 = 0 & c_0 = 0 \end{array}\right| \begin{array}{|c|c|}\hline 1 & 1 \\ \hline \multicolumn{1}{|c|}{2} & \\ \cline{1-1} \end{array}$$

Representation of CSF's as Gel'fand-Tsetlin basis

Assume we have built up this Paldus tableau up to the ith row:

$$\begin{vmatrix} a_i & b_i & c_i \\ \vdots & \vdots & \vdots \\ a_2 & b_2 & c_2 \\ a_1 & b_1 & c_1 \\ a_0 & b_0 & c_0 \end{vmatrix}$$

According to the rules, here $N_i = 2a_i + b_i$, $n_i = a_i + b_i + c_i$, and $S_i = 2b_i$.

When adding the next orbital ($n_{i+1} = n_i + 1$), we have four possibilities:

– adding no electrons: $N_{i+1} = N_i$ and $S_{i+1} = S_i$
– adding two electrons: $N_{i+1} = N_i + 2$ and $S_{i+1} = S_i$
– one electron and increasing the spin: $N_{i+1} = N_i + 1$ and $S_{i+1} = S_i + 1/2$
– one electron and decreasing the spin: $N_{i+1} = N_i + 1$ and $S_{i+1} = S_i - 1/2$

Representation of CSF's as Gel'fand-Tsetlin basis

Case 0, $N_{i+1} = N_i$ and $S_{i+1} = S_i$

$$\left|\begin{array}{ccc} a_i & b_i & c_i + 1 \\ a_i & b_i & c_i \\ \vdots & \vdots & \vdots \\ a_2 & b_2 & c_2 \\ a_1 & b_1 & c_1 \\ a_0 & b_0 & c_0 \end{array}\right|$$

Case 3, $N_{i+1} = N_i + 2$ and $S_{i+1} = S_i$

$$\left|\begin{array}{ccc} a_i + 1 & b_i & c_i \\ a_i & b_i & c_i \\ \vdots & \vdots & \vdots \\ a_2 & b_2 & c_2 \\ a_1 & b_1 & c_1 \\ a_0 & b_0 & c_0 \end{array}\right|$$

Representation of CSF's as Gel'fand-Tsetlin basis

Case 1, $N_{i+1} = N_i + 1$ and $S_{i+1} = S_i + 1/2$

$$\begin{vmatrix} a_i & b_i + 1 & c_i \\ a_i & b_i & c_i \\ \vdots & \vdots & \vdots \\ a_2 & b_2 & c_2 \\ a_1 & b_1 & c_1 \\ a_0 & b_0 & c_0 \end{vmatrix}$$

Case 2, $N_{i+1} = N_i + 2$ and $S_{i+1} = S_i - 1/2$

$$\begin{vmatrix} a_i + 1 & b_i - 1 & c_i \\ a_i & b_i & c_i \\ \vdots & \vdots & \vdots \\ a_2 & b_2 & c_2 \\ a_1 & b_1 & c_1 \\ a_0 & b_0 & c_0 \end{vmatrix}$$

Representation of CSF’s as Gel’fand-Tsetlin basis

There are only four cases when adding an orbital:

$$\begin{aligned}
\Delta a_i = 0, \Delta b_i = 0, \Delta c_i = 1 &\quad \rightarrow \quad d_i = 0 \\
\Delta a_i = 0, \Delta b_i = 1, \Delta c_i = 0 &\quad \rightarrow \quad d_i = 1 \\
\Delta a_i = 1, \Delta b_i = -1, \Delta c_i = 0 &\quad \rightarrow \quad d_i = 2 \\
\Delta a_i = 1, \Delta b_i = 0, \Delta c_i = 0 &\quad \rightarrow \quad d_i = 3
\end{aligned}$$

with $d_i = 2\Delta a_i - \Delta c_i + 1 = 3\Delta a_i + \Delta b_i$.

Thus, the $(a_i \; b_i \; c_i)$ triplets can be replaced by d_i, the *step number*:

$$\left|\begin{array}{ccc|c}
a_{i+1} & b_{i+1} & c_{i+1} & d_{i+1} \\
a_i & b_i & c_i & d_i \\
\vdots & \vdots & \vdots & \vdots \\
a_2 & b_2 & c_2 & d_2 \\
a_1 & b_1 & c_1 & d_1 \\
a_0 & b_0 & c_0 &
\end{array}\right|$$

Representation of CSF’s as Gel’fand-Tsetlin basis

Gelfand-Tsetlin basis is built up hierarchically:

The last step of the procedure: when adding the last orbital, we have to arrive at the desired number of electrons, N and spin, S.

$$\left|\begin{array}{ccc|c} a_n & b_n & c_n & d_n \\ \vdots & \vdots & \vdots & \vdots \\ a_i & b_i & c_i & d_i \\ \vdots & \vdots & \vdots & \vdots \\ a_2 & b_2 & c_2 & d_2 \\ a_1 & b_1 & c_1 & d_1 \\ a_0 & b_0 & c_0 & \end{array}\right|$$

with $N = 2a_n + b_n$, $S = 2b_n$ and $n = a_n + b_n + c_n$.

Representation of CSF's as Gel'fand-Tsetlin basis: the step vector

According to the above discussion, the step number (d_k) uniquely defines the change of the triplets of numbers $(\Delta a_k, \Delta b_k, \Delta c_k)$, thus when knowing $(a_{k-1}, b_{k-1}, c_{k-1})$, the values (a_k, b_k, c_k) can be obtained.

This means that the Paldus tableau can be reproduced by the so called *step vector*:

$$\left|\begin{array}{ccc} a_n & b_n & c_n \\ \vdots & \vdots & \vdots \\ a_i & b_i & c_i \\ \vdots & \vdots & \vdots \\ a_2 & b_2 & c_2 \\ a_1 & b_1 & c_1 \\ a_0 & b_0 & c_0 \end{array}\right| \rightarrow |d_1, d_2, ..., d_i, ..., d_n\rangle$$

Meaning of the step vector

$$|d_1, d_2, ..., d_i, ..., d_n\rangle$$

In the step vector there is an entry for every orbital:

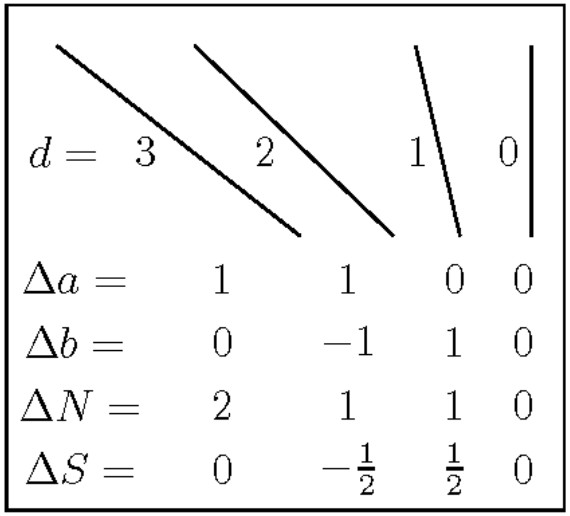
- $d_i = 0$ means the orbital is empty;
- $d_i = 1$ means the orbital is singly occupied, spin increases;
- $d_i = 2$ means the orbital is singly occupied, spin decreases;
- $d_i = 3$ means the orbital is doubly occupied.

Note, that this vector is very similar to an occupation number vector, and is very attempting to call $d_i = 1$ as α and $d_i = 2$ as β, **but this is not true in general**.

The definition above rather means that there always must be an "unpaired" $d_i = 1$ precede a $d_k = 2$ (since $S \geq 0$).

Graphical representation of Gel'fand-Tsetlin basis: Shavitt graph

Shavitt suggested a graphical representation to the step vectors. The idea is that the four different values of the step number are represented by lines of different slopes:



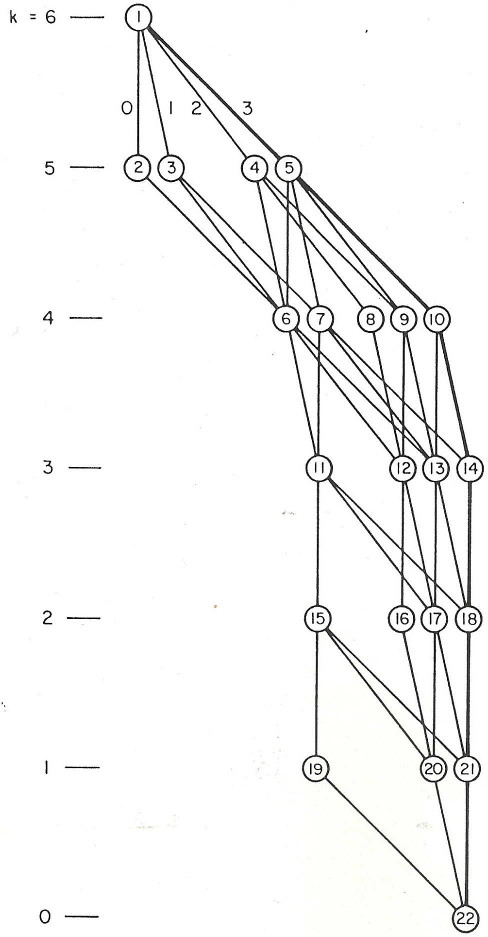
$d =$	3	2	1	0
$\Delta a =$	1	1	0	0
$\Delta b =$	0	-1	1	0
$\Delta N =$	2	1	1	0
$\Delta S =$	0	$-\frac{1}{2}$	$\frac{1}{2}$	0

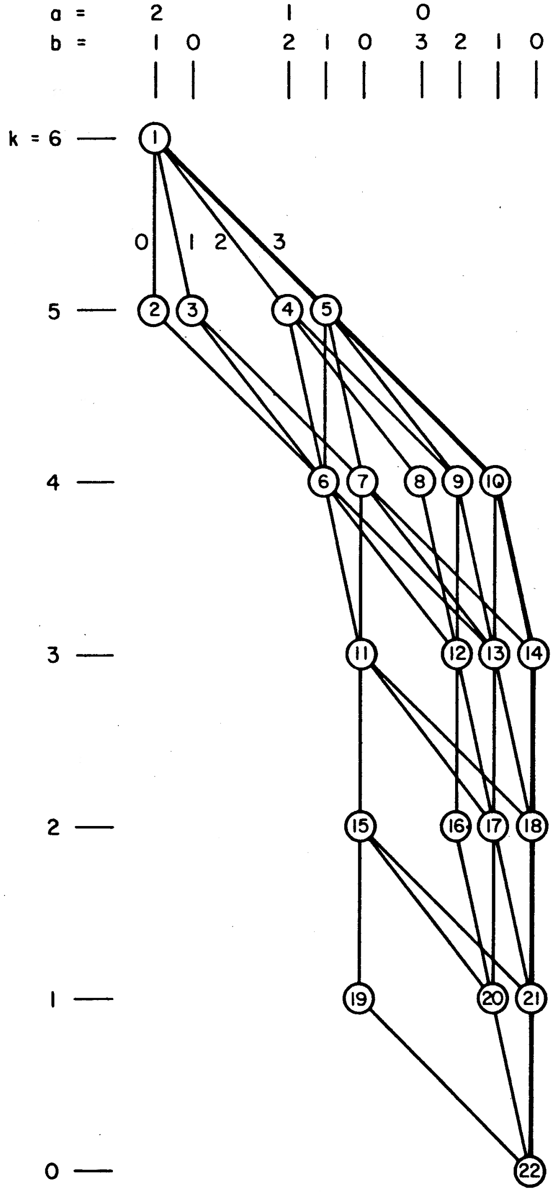
The slopes are chosen such that the vertical move by $d = 3$ equals that of $d = 1$ plus $d = 2$, i.e. whatever way we add two electrons, the vertical move is the same.

Graphical representation of Gel'fand-Tsetlin basis: Shavitt graph

The *step vectors* representing CSFs can be put into a graph:

- each CSF is represented by a path thru the graph
- orbitals are represented by the rows of the graph
- elements of the step vector are represented by arcs of different slope
- number of electrons and value of the spin is given by the vertical position in the graph
- bottom right corresponds to zero electrons ($S = 0$).
- top left corresponds to a given number of electrons and a given spin.
- therefore all CSFs representing a system with given number of electrons and given spin end in the same point.




a = 2 1 0
b = 1 0 2 1 0 3 2 1 0
k = 6
5
4
3
2
1
0
0 1 2 3
1
2
3
4
5
6
7
8
9
10
11
12
13
14
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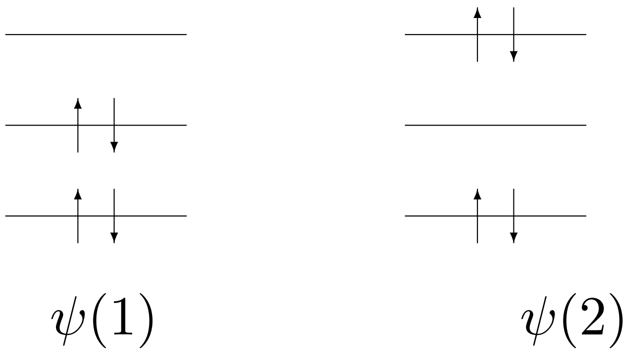
21
22

The Multireference Problem

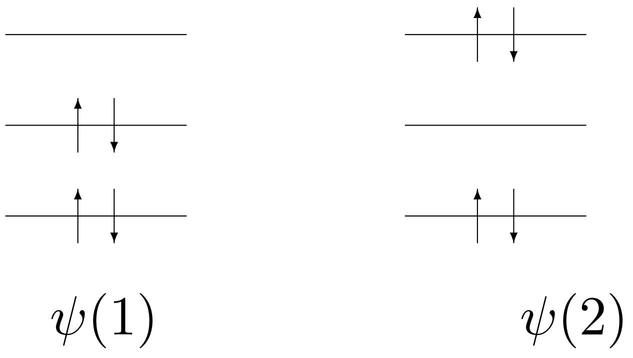
Example: ozone (O_3)



Both determinants are important for a qualitative description!

The Multireference Problem

Example: ozone (O_3)

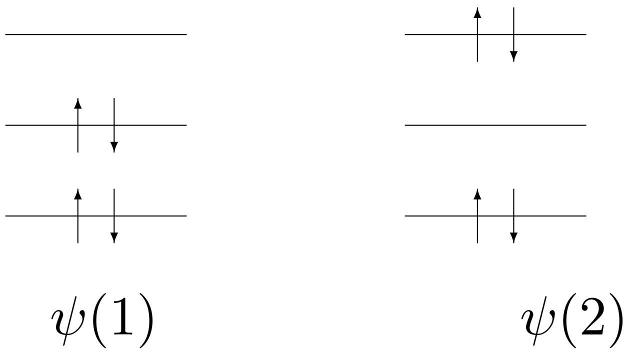


Both determinants are important for a qualitative description!

Both determinants should be used as reference in the truncated scheme!

The Multireference Problem

Example: ozone (O_3)



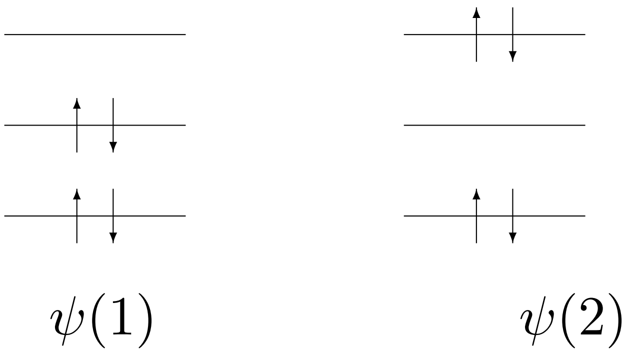
Both determinants are important for a qualitative description!

Both determinants should be used as reference in the truncated scheme!

$$\Phi_{\mathrm{MR-CISD}} = c(1)\psi(1) + c(2)\psi(2)$$

The Multireference Problem

Example: ozone (O_3)



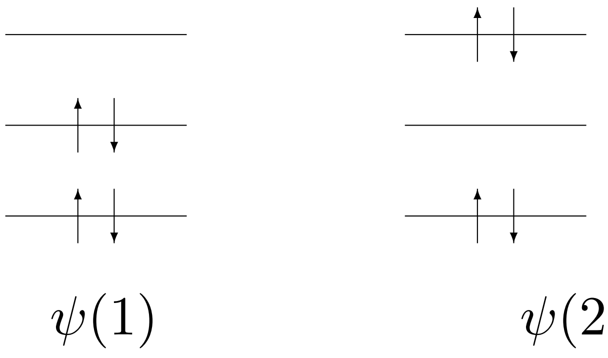
Both determinants are important for a qualitative description!

Both determinants should be used as reference in the truncated scheme!

$$\begin{aligned}\Phi_{\mathrm{MR-CISD}} &= c(1)\psi(1) + c(2)\psi(2) \\ &+ \sum_{ia} c(1)_i^a \psi(1)_i^a + \sum_{ia} c(2)_i^a \psi(2)_i^a\end{aligned}$$

The Multireference Problem

Example: ozone (O_3)



Both determinants are important for a qualitative description!

Both determinants should be used as reference in the truncated scheme!

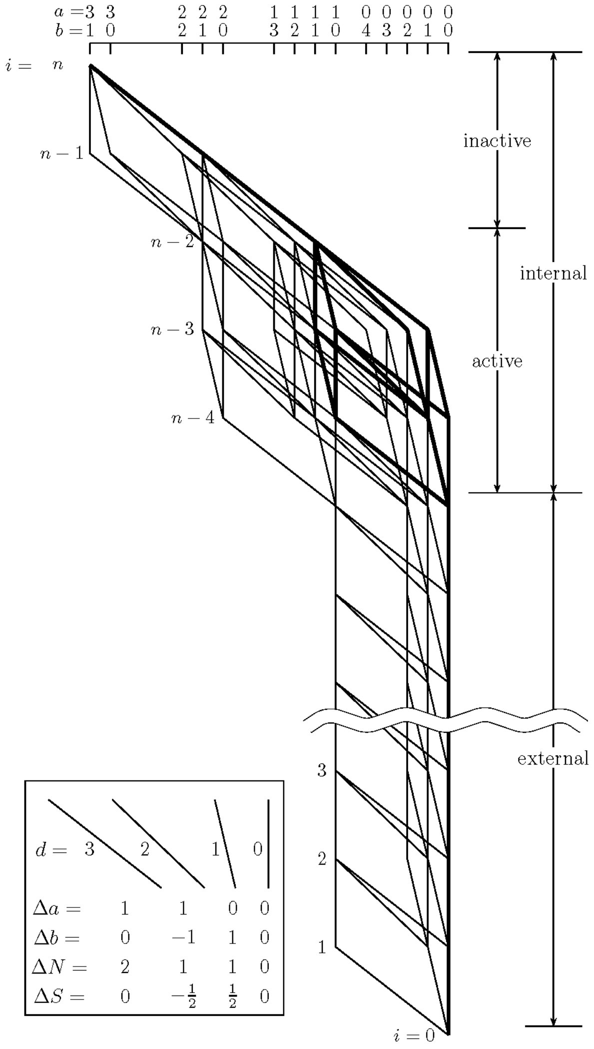
$$\begin{aligned}\Phi_{\mathrm{MR-CISD}} &= c(1)\psi(1) + c(2)\psi(2)\\ &+ \sum_{ia} c(1)_i^a\psi(1)_i^a + \sum_{ia} c(2)_i^a\psi(2)_i^a\\ &+ \sum_{i>j\ \ a>b} c(1)_{ij}^{ab}\psi(1)_{ij}^{ab} + \sum_{i>j\ \ a>b} c(2)_{ij}^{ab}\psi(2)_{ij}^{ab}\end{aligned}$$

The Multireference Problem

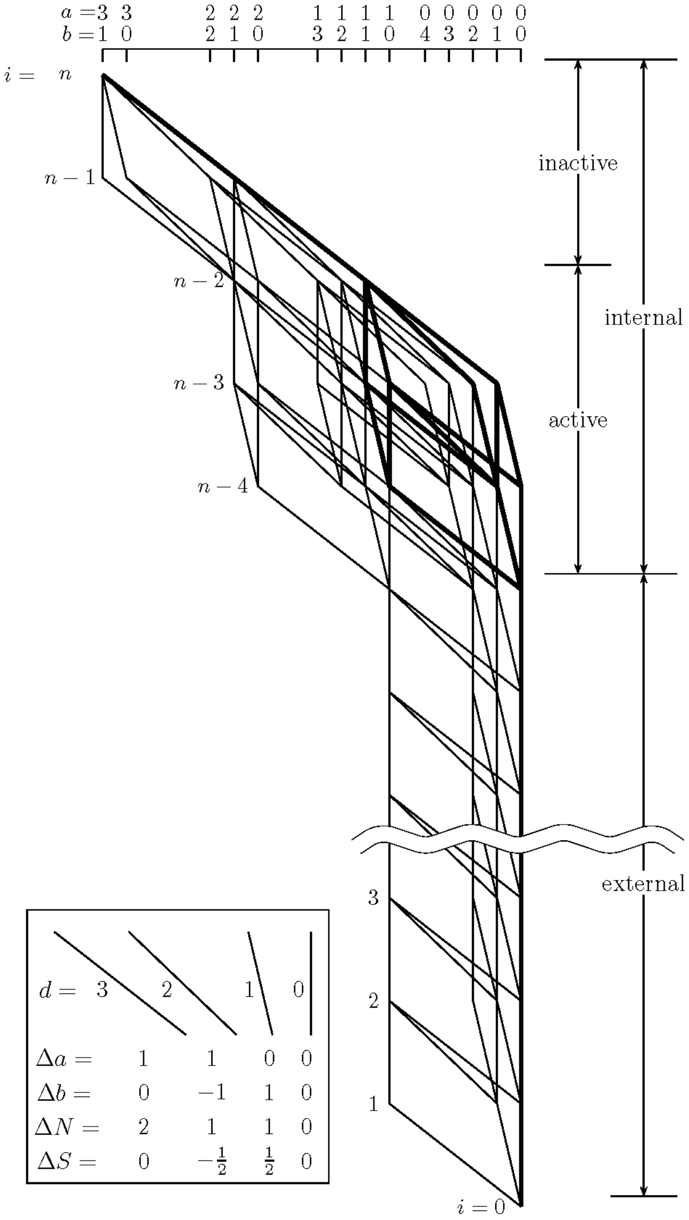
orbital type	reference	CI space
virtual	empty	empty, +1,+2
active **or open shell**	varying occupation	reference ±1,±2
double occupied **or closed shell**	double occupied	reference −1,−2
frozen core	double occupied	double occupied

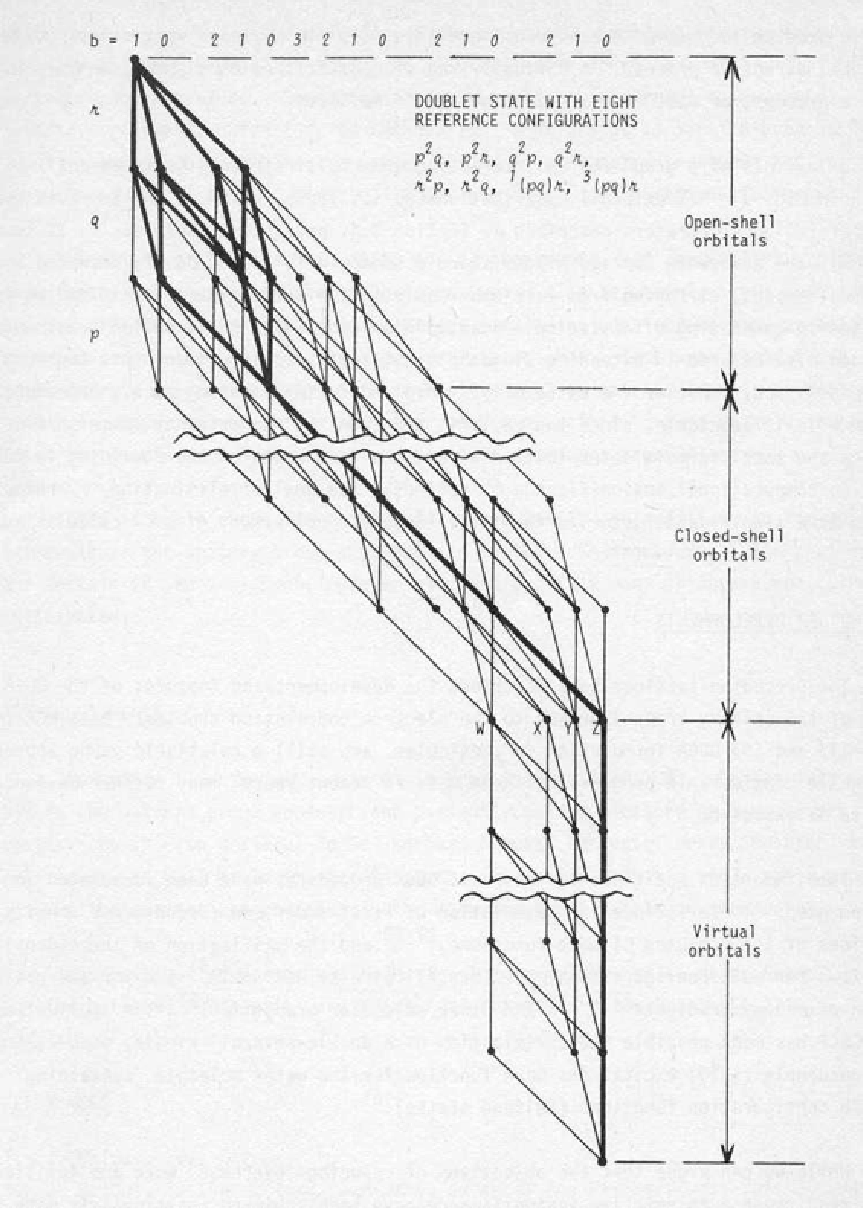
The Multireference Problem

Shavitt graph for MR-CISD wave function:



- Thick lines: reference CSFs
  - run together in the double occupied and virtual space
  - diverge in the “active” space
- both double occupied (inactive) and virtual (external) part of the graph has simple structure


a = 3 3 2 2 2 1 1 1 1 0 0 0 0 0
b = 1 0 2 1 0 3 2 1 0 4 3 2 1 0
i = n
n − 1
n − 2
n − 3
n − 4
inactive
internal
active
external
3
2
1
i = 0
d = 3 2 1 0
Δa = 1 1 0 0
Δb = 0 −1 1 0
ΔN = 2 1 1 0
ΔS = 0 −1/2 1/2 0


b = 1 0 2 1 0 3 2 1 0 2 1 0 2 1 0
r
q
p
DOUBLET STATE WITH EIGHT
REFERENCE CONFIGURATIONS
p^2q, p^2r, q^2p, q^2r,
r^2p, r^2q, $^1(pq)r$, $^3(pq)r$
Open-shell orbitals
Closed-shell orbitals
W
X
Y
Z
Virtual orbitals

Calculation of the Hamiltonian matrix elements

$$\begin{aligned} H_{ij} &= \langle \Phi_i | \hat{H} | \Phi_j \rangle \\ &= \sum_{rs} h_{rs} \langle \Phi_i | \hat{E}_{rs} | \Phi_j \rangle + \frac{1}{2} \sum_{rstu} \langle rt | su \rangle [\langle \Phi_i | \hat{E}_{rs} \hat{E}_{tu} | \Phi_j \rangle - \delta_{st} \langle \Phi_i | \hat{E}_{ru} | \Phi_j \rangle] \end{aligned}$$

All we need for the matrix elements are the

- integrals h_{rs} and $\langle rt|su \rangle$
- *coupling coefficients*: matrix elements of the generators of the unitary group
  - these can be calculated in the Gel'fand-Tsetlin basis using
    - Paldus tableau or
    - Shavitt graph.

Calculation of the one-electron matrix elements

The matrix elements between two walks on the Shavitt graph are needed:

$$\langle \Phi_i | \hat{E}_{rs} | \Phi_j \rangle \quad = \quad \langle \Phi_i | \hat{a}^\dagger_{r\alpha} \hat{a}_{s\alpha} + \hat{a}^\dagger_{r\beta} \hat{a}_{s\beta} | \Phi_j \rangle$$

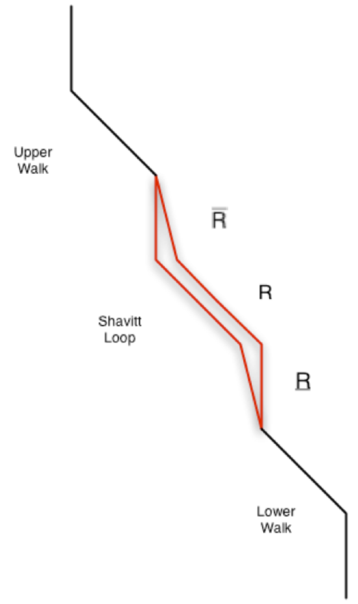
The creation and annihilation operators cause a change of occupation only on the rth and sth orbital:

Calculation of the one-electron matrix elements

The matrix elements between two walks on the Shavitt graph are needed:

$$\langle \Phi_i | \hat{E}_{rs} | \Phi_j \rangle \quad = \quad \langle \Phi_i | \hat{a}^\dagger_{r\alpha} \hat{a}_{s\alpha} + \hat{a}^\dagger_{r\beta} \hat{a}_{s\beta} | \Phi_j \rangle$$

The creation and annihilation operators cause a change of occupation only on the rth and sth orbital:



→ walks can differ only between these two orbitals

→ walks have to define a loop between levels r and s

→ otherwise the walks run together

Calculation of the one-electron matrix elements

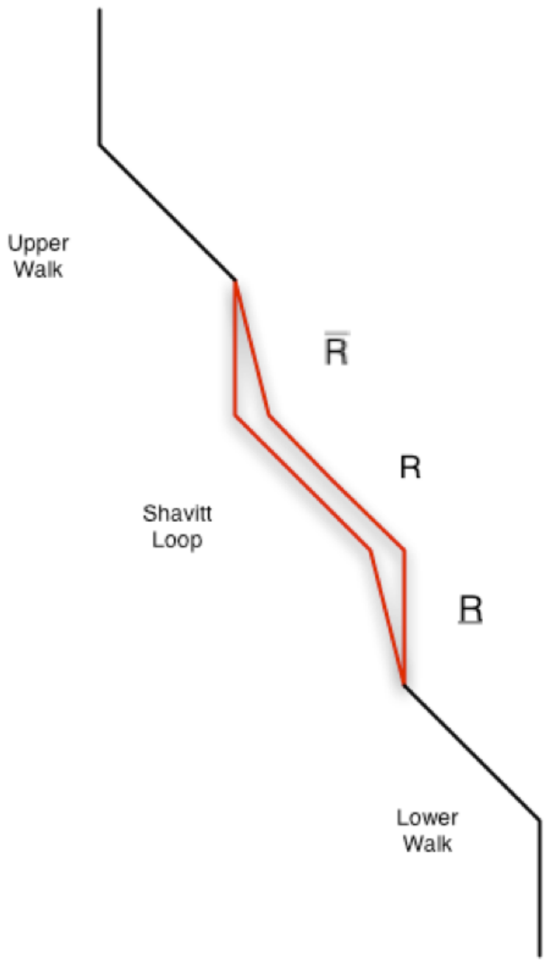
– walks of two CSFs diverge only for the range where their orbital occupations differ

– matrix elements depend only on the shape of the loop

– matrix element are calculated from the *segment values* $\bar{R}$, R and $\underline{\mathrm{R}}$.

Calculation of the matrix elements:

- identification of the loops
- identification of the segment values



Calculation of the two-electron matrix elements

The matrix elements between two walks on the Shavitt graph are needed:

$$\langle \Phi_i | \hat{E}_{rs} \hat{E}_{tu} | \Phi_j \rangle \quad = \quad \langle \Phi_i | (\hat{a}^\dagger_{r\alpha} \hat{a}_{s\alpha} + \hat{a}^\dagger_{r\beta} \hat{a}_{s\beta})(\hat{a}^\dagger_{t\alpha} \hat{a}_{u\alpha} + \hat{a}^\dagger_{t\beta} \hat{a}_{u\beta}) | \Phi_j \rangle$$

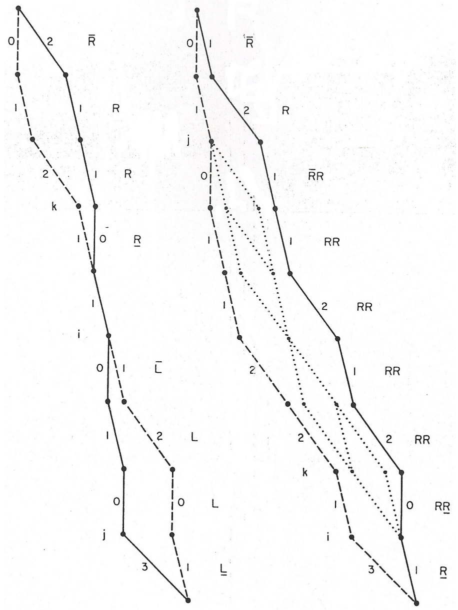
The creation and annihilation operators cause a change of occupation on rth, sth, tth and uth orbital:

Calculation of the two-electron matrix elements

The matrix elements between two walks on the Shavitt graph are needed:

$$\langle \Phi_i | \hat{E}_{rs} \hat{E}_{tu} | \Phi_j \rangle \quad = \quad \langle \Phi_i | (\hat{a}^\dagger_{r\alpha} \hat{a}_{s\alpha} + \hat{a}^\dagger_{r\beta} \hat{a}_{s\beta})(\hat{a}^\dagger_{t\alpha} \hat{a}_{u\alpha} + \hat{a}^\dagger_{t\beta} \hat{a}_{u\beta}) | \Phi_j \rangle$$

The creation and annihilation operators cause a change of occupation on rth, sth, tth and uth orbital:



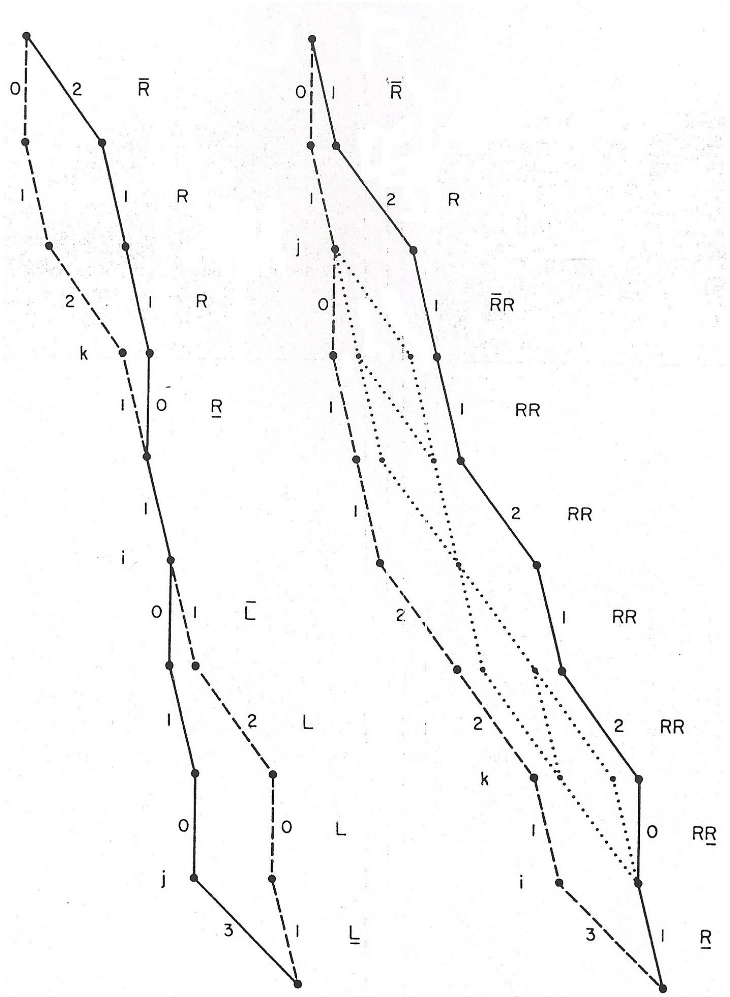
→ walks can differ only between these orbitals

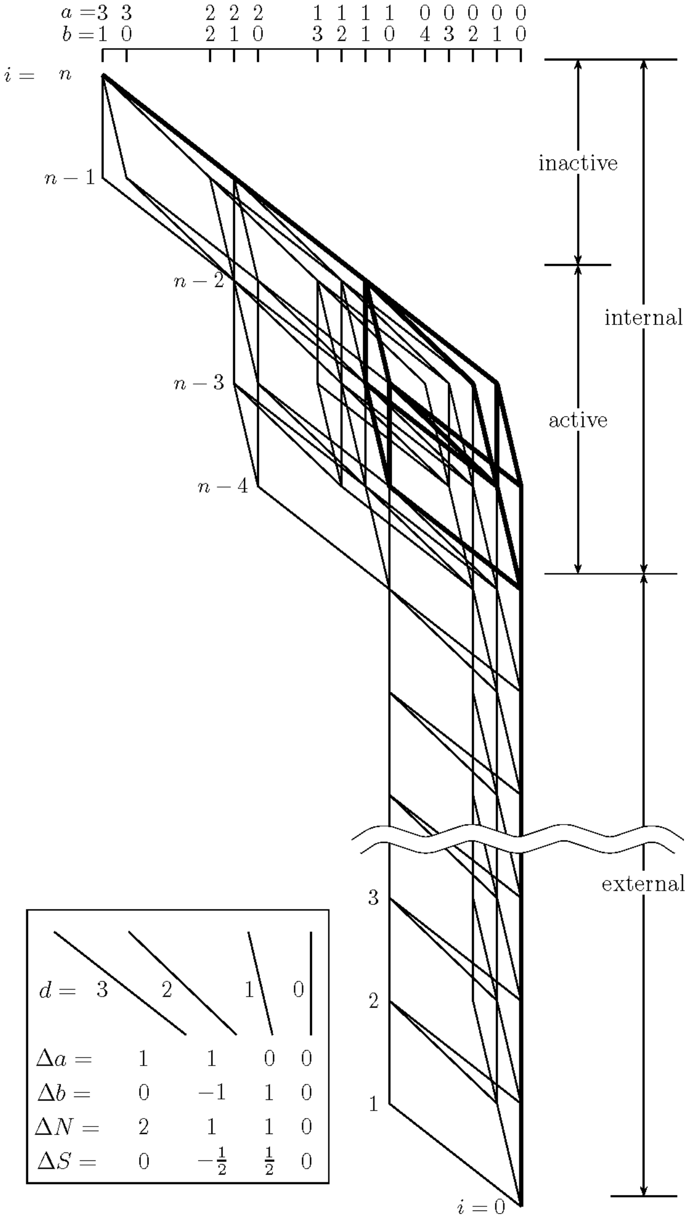
→ walks have to define loop(s) between these levels

→ otherwise the walks run together

Calculation of the Hamiltonian matrix elements

Two-electron matrix elements:





$d =$	3	2	1	0
$\Delta a =$	1	1	0	0
$\Delta b =$	0	-1	1	0
$\Delta N =$	2	1	1	0
$\Delta S =$	0	$-\frac{1}{2}$	$\frac{1}{2}$	0