Advanced Group Theoretical Methods in Theoretical Chemistry

Introduction to the Workshop on Theoretical Chemistry

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Outline

Introduction

Group theory is the mathematics of symmetry ...

'Group-theoretical deductions are usually quite easy to perform and the information so obtained concerning the solutions [of the Schrödinger equation (DA)], although not complete, often contains the essential physics.'

M Weissbluth, *Atoms and Molecules*, Academic Press, 1974, p 204

... and is hence an essential tool for our understanding.

How to specify the state of a quantum system?

A quantum state is completely specified by its eigenvalues associated with a complete set of commuting operators (CSCO).

PAM Dirac, *The Principles of Quantum Mechanics*, Oxford University Press, 1930
S Gasiorowicz, *Quantum Physics*, Wiley, 1974

H atom $|nlm\,{}^2L\rangle$ ($\widehat{H}$, $\widehat{L}^2$, $\widehat{L}_z$ are part of the CSCO for this case):

$$\widehat{H}\ |nlm\,{}^2L\rangle = -(2n^2)^{-1}\,E_{\mathrm{h}}\,|nlm\,{}^2L\rangle$$
$$\widehat{L}^2\,|nlm\,{}^2L\rangle = l(l+1)\,\hbar^2\,|nlm\,{}^2L\rangle\,, \qquad \widehat{L}_z\,|nlm\,{}^2L\rangle = m\,\hbar\,|nlm\,{}^2L\rangle$$

The CSCO contains $\widehat{H}$, $\widehat{\mathbf{L}}$ and $\widehat{\mathbf{A}}$ (Runge-Lenz vector). In this special case (one-electron atom), the symmetry group is isomorphic to $SO(4)$ (group of rotations of a 4D sphere).

Scheme of terms for four p electrons.

0	$+$	$-$	M Singlet		M Triplet	
··	·	·	0	^1S	0	^3P
·	··	·	$+1$	^1D	$+1$	
·	·	··	-1		-1	
	··	··	0			
··	··		$+2$			
··		··	-2			

H Hellmann, *Einführung in die Quantenchemie*, Deuticke, 1937, Springer, 2015, Tabelle 28

„Wenn man sich einmal das Schema […] notiert hat, kann man die interessierenden Energien fast unmittelbar hinschreiben. Es sei noch erwähnt, daß die Heranziehung des Vektormodells für diese Rechnung eigentlich eine Benutzung gruppentheoretischer Sätze bedeutet. Diese Sätze finden im Vektormodell eine überaus anschauliche und bequeme Formulierung. Wenn man das Vektormodell benutzt, muß man sich nur darüber klar sein, daß es sich dabei um eine bequeme Modellvorstellung zur Fixierung abstrakter und streng bewiesener mathematischer Sätze handelt.“

‘Once one has noticed the scheme […] one can write down the energies of interest almost immediately. It is worth to remark that the use of the vector coupling model for this calculation actually means the use of theorems of group theory. These theorems are expressed in a very obvious and convenient form by the vector coupling model. But when the vector coupling model is used one has to be aware that it is nothing more than a convenient model to express abstract and strictly proven mathematical theorems.’

H Hellmann, *Einführung in die Quantenchemie*, Deuticke, 1937, Springer, 2015, p 251f

Electron configurations and terms in atoms

${}_{3}$Li 2s^1 ($\binom{2}{1} = 2$ / **1** term)

$2S+1$	$2S$	S	#
2	1	1	2
			2

${}_{8}$O 2p^4 ($\binom{6}{4} = 15$ / **3** terms)

$2S+1$	$2S$	S	P	D	#
1	0	1	–	1	6
3	2	–	1	–	9
					15

... forms the simplest metal ...
... non-simple form of bonding ...

... forms open-shell system O_2 ...
... simple enough to learn from ...

EU Condon, GH Shortley, The Theory of Atomic Spectra, Cambridge Univ Press, 1935, p 208

Electron configurations and terms in atoms (contd.)

O atom: $1s^2\ 2s^2\ 2p^4 \ldots$

$\ldots$ (p_{+1}, p_0, p_{-1}) in $\mathbf{K}_h$:
^3P_g / ^1D_g / ^1S_g

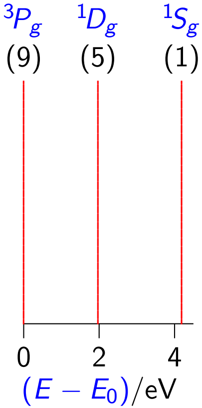
$\ldots$ (p_x, p_y, p_z) in $\mathbf{D}_{2h}$:
$^3B_{1g} \oplus {}^3B_{2g} \oplus {}^3B_{3g}$ /
$^1A_g(2) \oplus {}^1B_{1g} \oplus {}^1B_{2g} \oplus {}^1B_{3g}$ / ^1A_g

$\ldots$ (p_x, p_y, p_z) in $\mathbf{C}_{2v}$:
$^3B_1 \oplus {}^3B_2 \oplus {}^3A_2$ /
$^1A_1(2) \oplus {}^1B_1 \oplus {}^1B_2 \oplus {}^1A_2$ / $^1A_1$

$\ldots$ (p_x, p_y, p_z) in $\mathbf{C}_1$:
$^3A(3)$ / $^1A(5)$ / ^1A

… and **all results** — degeneracies, energies, occupation numbers, orbital radial parts — **are always the same!**

Density of states:



NIST Atomic Spectra Database (http://physics.nist.gov/asd)

Electron configurations and terms in atoms (contd.)

$_{22}$Ti $3d^2$ $4s^2$ ($\binom{10}{2} = 45$ / **5** terms)

$2S+1$	$2S$	S	P	D	F	G	#
1	0	1	–	1	–	1	15
3	2	–	1	–	1	–	30
							45

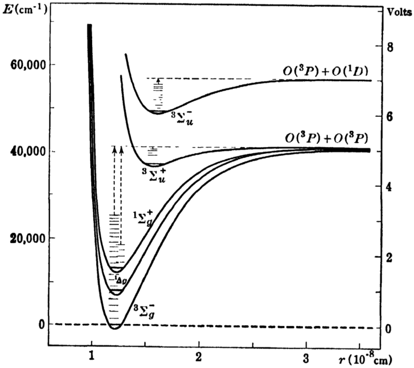
$_{25}$Mn^{2+} $3d^5$ ($\binom{10}{5} = 252$ / **16** terms)

$2S+1$	$2S$	S	P	D	F	G	H	I	#
2	1	1	1	3	2	2	1	1	150
4	3	–	1	1	1	1	–	–	96
6	5	1	–	–	–	–	–	–	6
									252

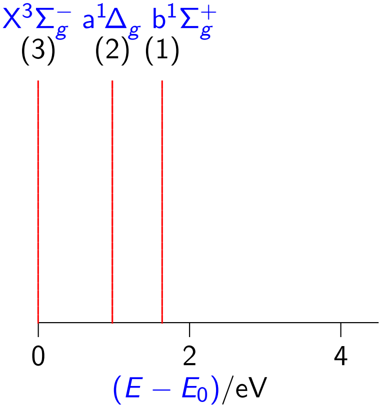
GAMESS inputs for SCF jobs for all terms from p^q and d^q, and for the high-spin terms from f^q ($0 < q < 4l + 2$, state-optimized or state-averaged) see: http://userpage.fu-berlin.de/∼dandrae/openshell/openls/openls.html

Electron configurations and terms in diatomics

O_2, low-lying bound states:



Density of states ($R \approx R_e$):



G Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, 1950, p 446 / KP Huber, G Herzberg, *Constants of Diatomic Molecules*, Van Nostrand, 1979 / PF Bernath, *Spectra of Atoms and Molecules*, 2nd ed, Oxford, 2005, p 326

Electron configurations and terms in diatomics (contd.)

O_2 $\pi_g{}^2$ ($\binom{4}{2} = 6$ / **3** terms)

$2S+1$	$2S$	Σ_g^+	Σ_g^-	Π_g	Δ_g	#
1	0	1	–	–	1	3
3	2	–	1	–	–	3
						6

Several bound states out of a **single electron configuration**

O ^{3}P + O ^{3}P (lowest asymptote: $9 \cdot 9 = 81$ / **18** terms)

$2S+1$	$2S$	Σ_g^+	Σ_g^-	Π_g	Δ_g	Σ_u^+	Σ_u^-	Π_u	Δ_u	#
1	0	2	–	1	1	–	1	1	–	9
3	2	–	1	1	–	2	–	1	1	27
5	4	2	–	1	1	–	1	1	–	45
										81

G Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, 1950, p 321 (Wigner-Witmer rules, 1928)
P Su et al, J Comput Chem **28** (2007) 185 (VB study)

Groups — General Aspects

General Aspects

Group. A group $\mathcal{G} = (S, *)$ results from a set of objects, S, and a law of combination, $*$ (usually called *multiplication*), when the following requirements are fulfilled:

(1) Closure:

$$a * b \in \mathcal{G} \qquad \forall a, b \in \mathcal{G}$$

(2) Multiplication is associative:

$$a * (b * c) = (a * b) * c \qquad \forall a, b, c \in \mathcal{G}$$

(3) Existence of a neutral element e:

$$a * e = e * a = a \qquad \forall a \in \mathcal{G}$$

(4) Existence of inverse elements:

$$a * a' = a' * a = e \qquad \forall a \in \mathcal{G}$$

Group element. Any member of the set forming a group.

Abelian group. [1] A group where multiplication is commutative:

$$a * b = b * a \qquad \forall a, b \in \mathcal{G}$$

[1] named after Niels Henrik Abel (1802–1829, Norwegian mathematician)

General Aspects (contd.)

Order of the group $\mathcal{G}$. The cardinality of the set S forming the group $\mathcal{G}$, usually denoted as h or $|\mathcal{G}|$.

- $h \in \mathbb{N}$: $\mathcal{G}$ is a **finite** group (h is the number of its elements).
  Example: Symmetry operations of a Platonic solid.
- $h = \infty$ (countably infinite): $\mathcal{G}$ is an **infinite discrete** group.
  Example: Translations of a crystal lattice.
- $h = \infty$ (continuous): $\mathcal{G}$ is a **continuous** group.
  Example: Rotations of a plane.

Order of the element a. The smallest positive integer n such that $a^n = e$.

Generators of a group. A smallest set of elements from which the complete group can be generated.

General Aspects (contd.)

Some more examples:

- integer numbers $\mathbb{Z}$ with addition (Abelian group, countably infinite order)
- rational numbers $\mathbb{Q} \setminus \{0\}$ with multiplication (Abelian group, countably infinite order)
- complex roots of unity $\{\exp(i2\pi k/n), i^2 = -1, k = 1, \ldots, n\}$ with multiplication (Abelian group, order n, a cyclic group)
- $Q = \{\pm 1, \pm i, \pm j, \pm k\}$ ($i^2 = j^2 = k^2 = -1$, $ij = k$) with multiplication (quaternion group, non-Abelian, order 8)
- permutations of n objects (symmetric group S_n, $n > 1$) (order $n!$, non-Abelian for $n > 2$)
- nonsingular $n \times n$ matrices with matrix multiplication (non-Abelian continuous group, important for representation theory)
- rotations of a sphere ($SO(3)$, special orthogonal group in $\mathbb{R}^3$, real orthogonal 3×3 matrices, non-Abelian continuous group)

General Aspects (contd.)

Subgroup of a group. A subgroup $\mathcal{H}$ of a group $\mathcal{G}$ is a subset which obeys the group requirements, usually denoted as $\mathcal{H} \leq \mathcal{G}$. Every group $\mathcal{G}$ has $\{e\}$ as trivial subgroup, and itself as improper subgroup. Lagrange's theorem (for finite groups): $|\mathcal{G}| = k \cdot |\mathcal{H}|$ $(k \in \mathbb{N})$.

Conjugate elements. Given $p, q, x \in \mathcal{G}$, then p and q are said to be conjugate if a similarity transform of p by x yields q (and *vice versa*):

$$x^{-1}\, p\, x = q \qquad \Leftrightarrow \qquad p = x\, q\, x^{-1}$$

Classes of conjugate elements. All elements conjugate to p, $x^{-1}\, p\, x$ $(x \in \mathcal{G})$, constitute a class of the group. For every group $\mathcal{G}$, the classes of conjugate elements provide a decomposition into disjoint subsets of group elements. In Abelian groups, every group element is in a class by itself.

General Aspects (contd.)

Mapping of groups. Given two groups $\mathcal{G}$ and $\mathcal{G}'$. A mapping $\varphi : \mathcal{G} \mapsto \mathcal{G}'$ assigns to each element $g \in \mathcal{G}$ an element $g' = \varphi(g) \in \mathcal{G}'$, such that every $g' \in \mathcal{G}'$ is the image of at least one $g \in \mathcal{G}$.

Homomorphism. If $\varphi(g_1)\varphi(g_2) = \varphi(g_1 g_2)$, for all $g_1, g_2 \in \mathcal{G}$, then φ is a homomorphic mapping of $\mathcal{G}$ on $\mathcal{G}'$: $\mathcal{G} \mapsto \mathcal{G}'$. Such a mapping is always *n*-to-one ($n > 1$).

Isomorphism. If the mapping φ is one-to-one (hence invertible), then it is an isomorphic mapping of $\mathcal{G}$ on $\mathcal{G}'$: $\mathcal{G} \simeq \mathcal{G}'$. Isomorphic groups have the *same* group structure, they are simply different realizations of the same abstract group.

General Aspects (contd.)

How many essentially different (i. e., non-isomorphic) finite groups exist for given order h?

h	N_a	N_n	N	h	N_a	N_n	N	h	N_a	N_n	N
1	1	0	1	8	3	2	5	15	1	0	1
2	1	0	1	9	2	0	2	16	5	9	14
3	1	0	1	10	1	1	2	17	1	0	1
4	2	0	2	11	1	0	1	18	2	3	5
5	1	0	1	12	2	3	5	19	1	0	1
6	1	1	2	13	1	0	1	20	2	3	5
7	1	0	1	14	1	1	2				

Table 1: Number of finite groups for small values of the order h [1].

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[1] On-Line Encyclopedia of Integer Sequences (https://oeis.org/), sequences A000001 ($N = N_\text{a} + N_\text{n}$), A000688 ($N_\text{a}$ number of Abelian groups) and A060689 (N_n number of non-Abelian groups)

Cayley tables for the finite groups with $1 \leq h \leq 6$:

Z_1	e
e	e

$Z_2 \simeq S_2$	e	a
e	e	a
a	a	e

Z_3	e	a	a^2
e	e	a	a^2
a	a	a^2	e
a^2	a^2	e	a

Z_4	e	a	a^2	a^3
e	e	a	a^2	a^3
a	a	a^2	a^3	e
a^2	a^2	a^3	e	a
a^3	a^3	e	a	a^2

V	e	a	b	ab
e	e	a	b	ab
a	a	e	$\boldsymbol{ab}$	b
b	b	ab	e	a
ab	ab	b	a	e

Z_5	e	a	a^2	a^3	a^4
e	e	a	a^2	a^3	a^4
a	a	a^2	a^3	a^4	e
a^2	a^2	a^3	a^4	e	a
a^3	a^3	a^4	e	a	a^2
a^4	a^4	e	a	a^2	a^3

Z_6	e	a	a^2	a^3	a^4	a^5
e	e	a	a^2	a^3	a^4	a^5
a	a	a^2	a^3	a^4	a^5	e
a^2	a^2	a^3	a^4	a^5	e	a
a^3	a^3	a^4	a^5	e	a	a^2
a^4	a^4	a^5	e	a	a^2	a^3
a^5	a^5	e	a	a^2	a^3	a^4

S_3	e	a	a^2	b	ba	ab
e	e	a	a^2	b	ba	ab
a	a	a^2	e	ab	b	ba
a^2	a^2	e	a	ba	ab	b
b	b	ba	ab	e	a	a^2
ba	ba	ab	b	a^2	e	a
ab	ab	b	ba	a	a^2	e

Cayley tables for the finite groups with $1 \le h \le 6$:

Z_1	e
e	e

$Z_2 \simeq S_2$	e	a
e	e	a
a	a	e

Z_3	e	a	a^2
e	e	a	a^2
a	a	a^2	e
a^2	a^2	e	a

Z_4	e	a	a^2	a^3
e	e	a	a^2	a^3
a	a	a^2	a^3	e
a^2	a^2	a^3	e	a
a^3	a^3	e	a	a^2

V	e	a	b	ab
e	e	a	b	ab
a	a	e	ab	b
b	b	ab	e	a
ab	ab	b	a	e

Z_5	e	a	a^2	a^3	a^4
e	e	a	a^2	a^3	a^4
a	a	a^2	a^3	a^4	e
a^2	a^2	a^3	a^4	e	a
a^3	a^3	a^4	e	a	a^2
a^4	a^4	e	a	a^2	a^3

Z_6	e	a	a^2	a^3	a^4	a^5
e	e	a	a^2	a^3	a^4	a^5
a	a	a^2	a^3	a^4	a^5	e
a^2	a^2	a^3	a^4	a^5	e	a
a^3	a^3	a^4	a^5	e	a	a^2
a^4	a^4	a^5	e	a	a^2	a^3
a^5	a^5	e	a	a^2	a^3	a^4

S_3	e	a	a^2	b	ba	ab
e	e	a	a^2	b	ba	ab
a	a	a^2	e	ab	b	ba
a^2	a^2	e	a	ba	ab	b
b	b	ba	ab	e	a	a^2
ba	ba	ab	b	a^2	e	a
ab	ab	b	ba	a	a^2	e

General Aspects (contd.)

Invariant subgroup (or normal subgroup or self-conjugate subgroup). Given a subgroup $\mathcal{H}$ of a group $\mathcal{G}$. If

$$x\mathcal{H} = \mathcal{H}x \qquad \Leftrightarrow \qquad x\mathcal{H}x^{-1} = \mathcal{H} \qquad \forall x \in \mathcal{G} \setminus \mathcal{H}$$

then $\mathcal{H}$ is an invariant subgroup of $\mathcal{G}$, written as $\mathcal{H} \lhd \mathcal{G}$. An invariant subgroup $\mathcal{H}$ of $\mathcal{G}$ consists of complete classes of $\mathcal{G}$.

Simple group. A simple group $\mathcal{G}$ has only the trivial subgroup of order one (containing the identity element of the group) and itself (as improper subgroup) as invariant subgroups:

$$\{e\} \lhd \mathcal{G} \qquad \text{and} \qquad \mathcal{G} \lhd \mathcal{G}\,.$$

The role of simple groups in group theory is comparable to the role of the prime numbers in number theory.

General Aspects (contd.)

Classification theorem of finite simple groups.
Every finite simple group is isomorphic to one of the following groups:
- A cyclic group of prime order, Z_p
- An alternating group of degree at least 5, A_n ($n > 4$)
- A simple group of Lie type [1] over a finite field (16 infinite families)
- The 27 sporadic simple groups.

A_n ($n > 4$) is a simple group ⇒ Important consequence:
Non-existence of *general* algebraic solution for polynomial equations of degree 5 or higher (Abel–Ruffini theorem, 1799/1823) [2,3]

Direct product of groups. Given two finite groups $\mathcal{G}_a = (\{a_1 = e, a_i\}, *)$ ($i = 2, \ldots, h_a$) and $\mathcal{G}_b = (\{b_1 = e, b_j\}, *)$ ($j = 2, \ldots, h_b$), for which holds $a_i * b_j = b_j * a_i$ for all a_i, b_j. Then the direct product group $\mathcal{G}$ is defined as

$$\mathcal{G} = \mathcal{G}_a \times \mathcal{G}_b = (\{a_i * b_j\}, *) \,.$$

The order of $\mathcal{G}$ is $h = h_a h_b$. The groups $\mathcal{G}_a$ and $\mathcal{G}_b$ are invariant subgroups of $\mathcal{G}$. Important special cases include direct products of pure rotation groups ($\mathbf{C}_n$, $\mathbf{D}_n$, $\mathbf{T}$, $\mathbf{O}$, $\mathbf{I}$) with $\mathbf{C}_s$ or $\mathbf{C}_i$.

[1] named after Sophus Lie (1842–1899, Norwegian mathematician)
[2] named after Paolo Ruffini (1765–1822, Italian mathematician)
[3] for more details see P Pesic: *Abel's Proof*; MIT Press, 2003

General Aspects (contd.)

Anything missing?

Well, a lot — for example:

Cosets (left cosets, right cosets, double cosets), automorphism, factor group, . . .

Representation Theory (reducible representations, irreducible representations [IRs], characters, character tables, Kronecker products, simply reducible groups, Clebsch–Gordan coefficients, projection operators, Wigner–Eckart theorem, . . .)

Angular Momentum Theory

. . .

Finite Groups

An example of a permutation group

The elements of the symmetric group S_3 (the $3! = 6$ permutations of 3 objects):

group element	two-line notation	disjoint cycle notation	cycle structure	matrix notation	trace of matrix
e	$\begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}$	(1)(2)(3)	f_1^3	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	3
a	$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}$	(123)	f_3	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	0
a^2	$\begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}$	(132)	f_3	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	0
b	$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}$	(12)(3)	$f_1 f_2$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	1
ba	$\begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}$	(1)(23)	$f_1 f_2$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	1
ab	$\begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}$	(13)(2)	$f_1 f_2$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	1

Subgroups: $\{e\}$, $\{e, a, a^2\}$, $\{e, b\}$, $\{e, ba\}$, $\{e, ab\}$, S_3 / Classes: $\{e\}$, $\{a, a^2\}$, $\{b, ba, ab\}$

Importance of permutation groups, in particular of the symmetric groups S_n:

Cayley's theorem [1]. Any group of order $h = n$ is isomorphic to a subgroup of the symmetric group S_n.

Pauli exclusion principle. The total wave function $|\Psi\rangle$ for a system of n indistinguishable fermions [bosons] has to transform – under permutations of these particles – in accordance with the totally antisymmetrical [totally symmetrical] irreducible representation (IR) of S_n (both IRs are one-dimensional).

Quantum mechanical treatment of nuclear motion makes use of the **complete nuclear permutation and inversion** (CNPI) group, e. g. ethene, C_2H_4: $\mathcal{G} = S_4^{(H)} \times S_2^{(C)} \times \{\widehat{E}, \widehat{E}^*\}^a$ (the order of this group is $h = 4! \cdot 2! \cdot 2 = 96$).

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[1] named after Arthur Cayley (1821–1895, British mathematician)

[a] $\widehat{E}$ identity ($\widehat{E}\mathbf{r} = \mathbf{r}$), $\widehat{E}^*$ space inversion ($\widehat{E}^*\mathbf{r} = -\mathbf{r}$).

Symmetry Operations and Point Groups

Symmetry operation. An operation that carries an object into a situation indistinguishable from its situation before application of the operation.

Symmetry element. A geometrical object (point, line, plane), or a combination thereof, with respect to which certain symmetry operations may be carried out.

Important note: Symmetry *elements* (e. g. inverison centre, axes, planes) are not group *elements*, but symmetry operations (e. g. rotations, reflections) are.

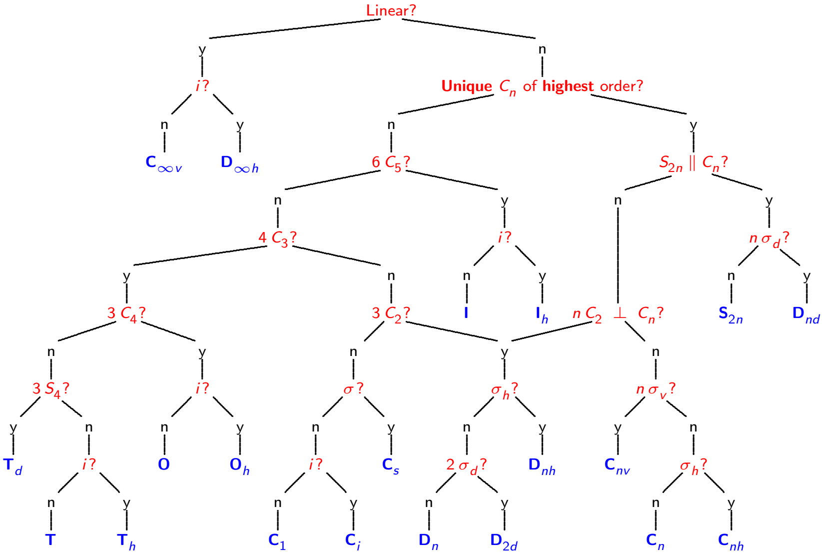
Point group. A group formed by the set of symmetry operations of a rigid physical object. The two kinds of symmetry operations in point groups are **proper rotations** (physically feasible) and **improper rotations** (roto-reflections or roto-inversions, not physically feasible).

Symbol	Generators	Symmetry elements	Order	Comments
$\mathbf{C}_1$	$\widehat{E}$	none	1	no symmetry
$\mathbf{C}_s$	$\widehat{\sigma}$	σ	2	$\mathbf{C}_s = \mathbf{C}_{1h} = \mathbf{C}_{1v} = \mathbf{S}_1$
$\mathbf{C}_i$	$\widehat{i}$	i	2	$\mathbf{C}_i = \mathbf{S}_2$
$\mathbf{C}_n$	$\widehat{C}_n$	C_n	n	$n = 2, 3, 4, \ldots$; Abelian
$\mathbf{S}_{2n}$	$\widehat{S}_{2n}$	C_n, S_{2n}	$2n$	Abelian
$\mathbf{C}_{nh}$	$\widehat{C}_n$, $\widehat{\sigma}_h$	C_n, σ_h, S_n	$2n$	Abelian
$\mathbf{C}_{nv}$	$\widehat{C}_n$, $\widehat{\sigma}_v$	C_n, $n\sigma_v$	$2n$	regular *n*-gonal pyramid
$\mathbf{D}_n$	$\widehat{C}_n$, $\widehat{C}_2'$	C_n, nC_2'	$2n$	
$\mathbf{D}_{nh}$	$\widehat{C}_n$, $\widehat{C}_2'$, $\widehat{\sigma}_h$	C_n, nC_2', S_n, σ_h, $n\sigma_v$	$4n$	regular *n*-gonal prism
$\mathbf{D}_{nd}$	$\widehat{C}_n$, $\widehat{C}_2'$, $\widehat{\sigma}_d$	C_n, nC_2', S_{2n}, $n\sigma_d$	$4n$	
$\mathbf{C}_{\infty v}$	$\widehat{C}_\infty$, $\widehat{\sigma}_v$	C_∞, $\infty\sigma_v$	∞	Full sym. of cone
$\mathbf{D}_{\infty h}$	$\widehat{C}_\infty$, $\widehat{C}_2'$, $\widehat{\sigma}_h$	C_∞, $\infty\sigma_v$, S_∞, $\infty C_2'$	∞	Full sym. of cylinder
$\mathbf{T}$	$\widehat{C}_3^{(111)}$, $\widehat{C}_2^{(z)}$	$4C_3$, $3C_2$	12	Rotations of $\{3, 3\}$
$\mathbf{T}_h$	$\widehat{C}_3^{(111)}$, $\widehat{C}_2^{(z)}$, $\widehat{i}$	$4C_3$, $3C_2$, $4S_6$, $3\sigma_v$	24	
$\mathbf{T}_d$	$\widehat{C}_3^{(111)}$, $\widehat{S}_4^{(z)}$	$4C_3$, $3C_2$, $3S_4$, $6\sigma_d$	24	Full symmetry of $\{3, 3\}$
$\mathbf{O}$	$\widehat{C}_3^{(111)}$, $\widehat{C}_4^{(z)}$	$4C_3$, $3C_4$, $6C_2$	24	Rotations of $\{3, 4\}$
$\mathbf{O}_h$	$\widehat{C}_3^{(111)}$, $\widehat{C}_4^{(z)}$, $\widehat{i}$	$4C_3$, $3C_4$, $6C_2$, $3S_4$, $4S_6$, $3\sigma_h$, $6\sigma_d$	48	Full symmetry of $\{3, 4\}$
$\mathbf{I}$	$\widehat{C}_3^{(ico)}$, $\widehat{C}_5^{(z)}$	$6C_5$, $10C_3$, $15C_2$	60	Rotations of $\{3, 5\}$
$\mathbf{I}_h$	$\widehat{C}_3^{(ico)}$, $\widehat{C}_5^{(z)}$, $\widehat{i}$	$6C_5$, $10C_3$, $15C_2$, $12S_{10}$, $10S_6$, 15σ	120	Full symmetry of $\{3, 5\}$

Table 2: Point groups in three-dimensional space (except $\mathbf{K}$ and $\mathbf{K}_h$) [1].

[1] adapted from JA Salthouse, MJ Ware: *Point group character tables and related data*. Cambridge, 1972, p 16

An algorithm to determine the point group from symmetry elements[1]



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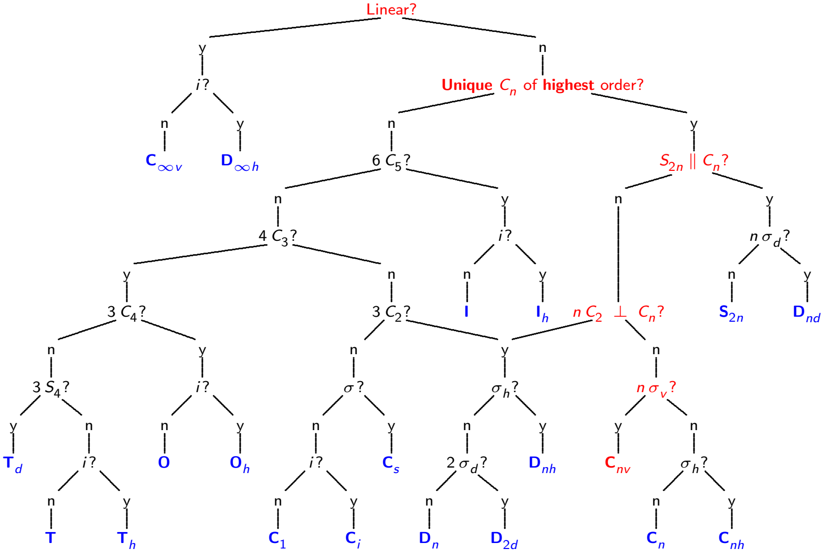
[1] JA Salthouse, MJ Ware: *Point group character tables and related data*. Cambridge, 1972, p 29

Determination of point groups $\mathbf{C}_{nv}$[1] (Examples: H_2O [$n = 2$], NH_3 [$n = 3$])



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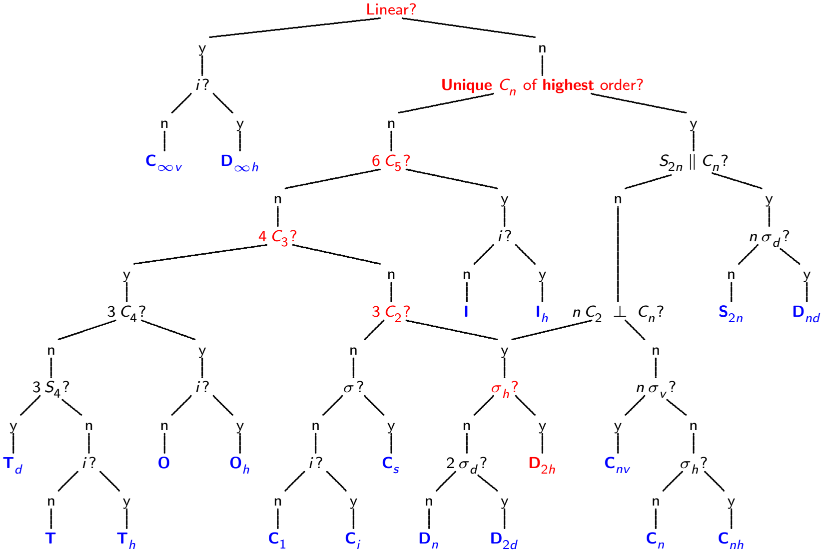
[1] JA Salthouse, MJ Ware: *Point group character tables and related data*. Cambridge, 1972, p 29

Determination of the point group $\mathbf{D}_{2h}$[1] (Example: C_2H_4)



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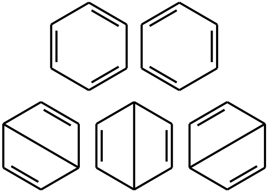
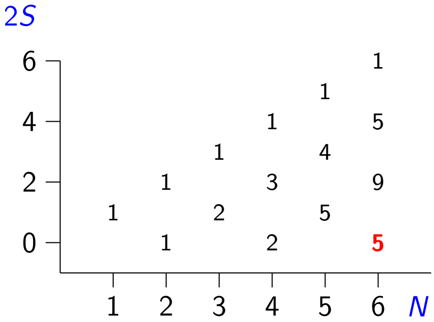
[1] JA Salthouse, MJ Ware: *Point group character tables and related data*. Cambridge, 1972, p 29

Benzene



Kekulé structures (top) and Dewar structures (bottom)

Branching diagram for electrons (up to $N = 6$ electrons) ▶



$\mathbf{D}_{6h}$	$\hat{E}$	$2\hat{C}_6$	$2\hat{C}_3$	$\hat{C}_2$	$3\hat{C}_2'$	$3\hat{C}_2''$	$\hat{i}$	$2\hat{S}_3$	$2\hat{S}_6$	$\hat{\sigma}_h$	$3\hat{\sigma}_d$	$3\hat{\sigma}_v$
Γ_K^{red}	2	0	2	0	0	2	0	2	0	2	2	0
Γ_D^{red}	3	0	0	3	1	1	3	0	0	3	1	1

$$\Gamma_K^{red} = A_{1g} \oplus B_{2u}$$
$$\Gamma_D^{red} = A_{1g} \oplus E_{2g}$$

⇒

Both the Kekulé structures and the Dewar structures contribute to the electronic grond state $\widetilde{X}\ {}^1A_{1g}$ (S_0) of benzene, but the Dewar structures do not contribute to the lowest excited singlet state ${}^1B_{2u}$ (S_1).

Benzene (contd) — Counting derivatives $C_6H_{6-k}X_k$ [1,2]

Symmetry operations (from either $\mathbf{D}_6$ or $\mathbf{D}_{6h}$) induce permutations among the positions of the H atoms

Cycle index $Z_{\text{rot}} = Z_{\text{full}}$ (summarizes permutational structure of parent compound), here:

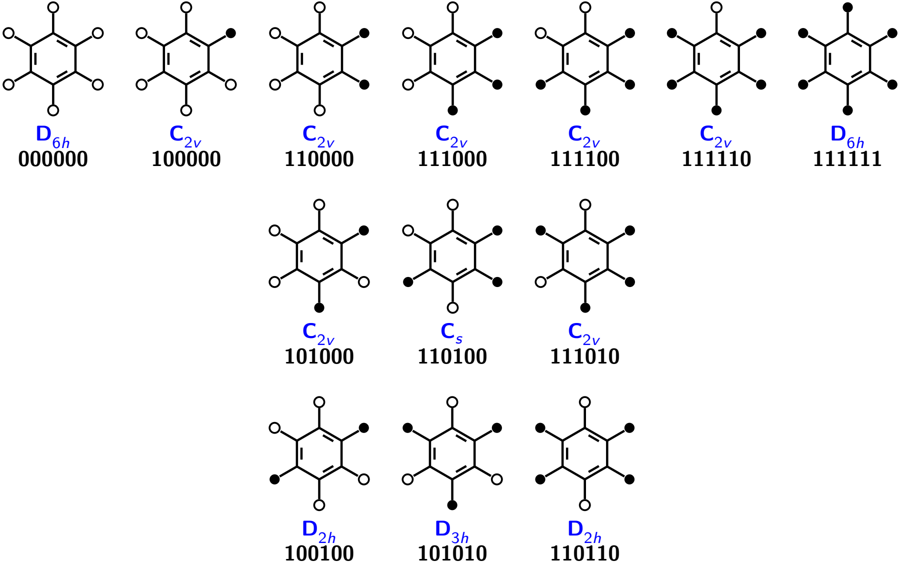
$$Z = \frac{1}{12}\left(f_1^6 + 3f_1^2 f_2^2 + 4f_2^3 + 2f_3^2 + 2f_6\right)$$

Substitution of f_i by figure counting function (here: $f_i = 1 + x^i$) yields counting polynomial $G(x)$, here:

$$G(x) = \sum_k a_k x^k = 1 + x + 3x^2 + 3x^3 + 3x^4 + x^5 + x^6$$

[1] G Pólya, *Acta Math.* **68** (1937) 145–254

[2] G Pólya, RC Read, *Combinatorial Enumeration of Groups, Graphs, and Chemical Compounds*; Springer, 1987



$\mathbf{D}_{6h}$ 000000

$\mathbf{C}_{2v}$ 100000

$\mathbf{C}_{2v}$ 110000

$\mathbf{C}_{2v}$ 111000

$\mathbf{C}_{2v}$ 111100

$\mathbf{C}_{2v}$ 111110

$\mathbf{D}_{6h}$ 111111

$\mathbf{C}_{2v}$ 101000

$\mathbf{C}_{s}$ 110100

$\mathbf{C}_{2v}$ 111010

$\mathbf{D}_{2h}$ 100100

$\mathbf{D}_{3h}$ 101010

$\mathbf{D}_{2h}$ 110110

The complete set of benzene derivatives $C_6H_{6-k}X_k$ $(0 \leq k \leq 6)$, showing their structural formulas, point group symbols and encoding strings [1].

[1] AP Bhati, D Andrae, submitted for publication (2015)

Magnitude of molecular static electric dipole moments μ (in Debye) of polar benzene derivatives $C_6H_{6\text{-}k}X_k$ ($1 \leq k \leq 5$, X = F or X = Cl) [1].

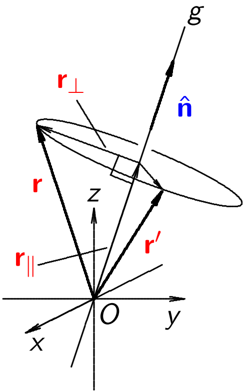
k	benzene derivative (point group)	encoding string	μ^a	
			X = F	X = Cl
1	C_6H_5X ($\mathbf{C}_{2v}$)	**100000**	1.34 (1.60)	1.91 (1.69)
2	1,2-$C_6H_4X_2$ ($\mathbf{C}_{2v}$)	**110000**	2.25 (2.46)	2.75 (2.50)
	1,3-$C_6H_4X_2$ ($\mathbf{C}_{2v}$)	**101000**	1.33 (1.51)	1.79 (1.72)
3	1,2,3-$C_6H_3X_3$ ($\mathbf{C}_{2v}$)	**111000**	2.57	2.79
	1,2,4-$C_6H_3X_3$ ($\mathbf{C}_s$)	**110100**	1.27 (1.40)	1.39
4	1,2,3,4-$C_6H_2X_4$ ($\mathbf{C}_{2v}$)	**111100**	2.19 (2.42)	2.09
	1,2,3,5-$C_6H_2X_4$ ($\mathbf{C}_{2v}$)	**111010**	1.24 (1.46)	1.00
5	1,2,3,4,5-C_6HX_5 ($\mathbf{C}_{2v}$)	**111110**	1.24	0.93

[1] AP Bhati, D Andrae, submitted for publication (2015)

[a] calcd. from KS-DFT, B3-LYP, 6-31G** (exptl. values in parentheses, from CRC Hdbk of Chemistry and Physics)

Continuous Groups

Proper and improper rotations in 3D



$$\mathbf{r} = \mathbf{r}_\parallel + \mathbf{r}_\perp,\ \mathbf{r}_\parallel = \lambda\hat{\mathbf{n}}$$

$$\hat{\mathbf{n}} = (n_1, n_2, n_3)^T,\ |\hat{\mathbf{n}}| = 1$$

Parametrization with angle φ and unit vector $\hat{\mathbf{n}}$:

(a)
Proper rotations $\widehat{R}_+(\varphi\hat{\mathbf{n}})$:

$$\begin{aligned}\mathbf{r}' &= \widehat{R}_+(\varphi\hat{\mathbf{n}})\,\mathbf{r}\\ &= a\,\mathbf{r} + b\,\hat{\mathbf{n}} \times \mathbf{r} + (c-a)\,\hat{\mathbf{n}}(\hat{\mathbf{n}} \cdot \mathbf{r})\\ &= \cos(\varphi)\,\mathbf{r} + \frac{\sin(\varphi)}{\varphi}\,\varphi\hat{\mathbf{n}} \times \mathbf{r} + \frac{1-\cos(\varphi)}{\varphi^2}\,\varphi\hat{\mathbf{n}}(\varphi\hat{\mathbf{n}} \cdot \mathbf{r})\end{aligned}$$

$(a = \cos(\varphi),\ b = \sin(\varphi),\ c = +1)$

Identity: $\widehat{E} = \widehat{R}_+(\mathbf{0})$

(b)
Improper rotations $\widehat{R}_-(\varphi\hat{\mathbf{n}})$:
as above, but with $c = -1$

Proper and improper rotations in 3D (contd)

Parametrization with angle φ $(0 \leq \varphi \leq \pi)$ and direction to the pole $\hat{\mathbf{n}}$:

$$\widehat{R}_{\pm}(\varphi\hat{\mathbf{n}}) = \begin{pmatrix} a + (c-a){n_1}^2 & (c-a)n_1 n_2 - b\, n_3 & (c-a)n_1 n_3 + b\, n_2 \\ (c-a)n_2 n_1 + b\, n_3 & a + (c-a){n_2}^2 & (c-a)n_2 n_3 - b\, n_1 \\ (c-a)n_3 n_1 - b\, n_2 & (c-a)n_3 n_2 + b\, n_1 & a + (c-a){n_3}^2 \end{pmatrix}$$

$$\det(\widehat{R}_{\pm}) = c = \pm 1\,, \qquad \chi(\widehat{R}_{\pm}) = c + 2\,a = \pm 1 + 2\cos(\varphi)$$

Alternative parametrization of proper rotations with quaternions[a] [1]:

$$\varphi\hat{\mathbf{n}} \mapsto [\lambda, \mathbf{\Lambda}] \qquad \text{with} \;\; \lambda = \cos(\varphi/2)\,,\; \mathbf{\Lambda} = \sin(\varphi/2)\hat{\mathbf{n}} \;\; (\lambda^2 + \mathbf{\Lambda}\cdot\mathbf{\Lambda} = 1)$$

Multiplication rule:

$$[\lambda_i, \mathbf{\Lambda}_i][\lambda_j, \mathbf{\Lambda}_j] = [\lambda_k, \mathbf{\Lambda}_k] \qquad \text{where} \;\; \lambda_k = \lambda_i\lambda_j - \mathbf{\Lambda}_i\cdot\mathbf{\Lambda}_j \;\; \text{and} \;\; \mathbf{\Lambda}_k = \lambda_i\mathbf{\Lambda}_j + \lambda_j\mathbf{\Lambda}_i + \mathbf{\Lambda}_i \times \mathbf{\Lambda}_j$$

$\rightsquigarrow$ The group of proper rotations in 3D is not Abelian (because $\mathbf{\Lambda}_i \times \mathbf{\Lambda}_j \neq \mathbf{\Lambda}_j \times \mathbf{\Lambda}_i$)!

Warning: In single groups, rather than double groups, the result $[\lambda_k, \mathbf{\Lambda}_k]$ may be mutliplied by ±1 without any change! The double group $\mathcal{G}^*$ of $\mathcal{G}$ is obtained when $\widehat{\widehat{E}} = \widehat{R}_{+}(2\pi\hat{\mathbf{n}})$ is distinguished from the identity $\widehat{E} = \widehat{R}_{+}(4\pi\hat{\mathbf{n}})$ (any $\hat{\mathbf{n}}$).

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[1] SL Altmann, P Herzig, *Point-Group Theory Tables*, 2nd corr. ed., 2011

[a] Quaternions $\mathbb{H} = \{q = a + ib + jc + kd = [a, (b, c, d)] | a, b, c, d \in \mathbb{R}; i^2 = j^2 = k^2 = -1, ij = k\}$

Transformation of Scalar Functions

Let $\mathbf{r}' = \widehat{R}\mathbf{r}$. How is a scalar function $f(\mathbf{r})$ then being transformed? The required condition is (this demands equality of function values)

$$(\widehat{O}_R f)(\mathbf{r}') = f(\mathbf{r}) = f(\widehat{R}^{-1}\mathbf{r}')\,,$$

or in short simply

$$(\widehat{O}_R f)(\mathbf{r}) = f(\widehat{R}^{-1}\mathbf{r})\,.$$

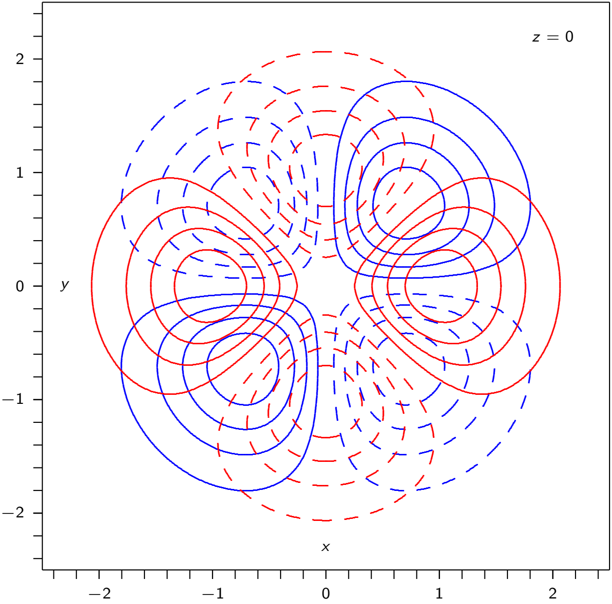
Example:

What happens to $f(\mathbf{r}) = f(x,y,z) = x\,y\,\exp\left(-r^2\right)$ under the counterclockwise rotation around the z axis ($\hat{\mathbf{n}} = (0,0,1)^T$) through $\phi = \pi/4 = 2\pi/8$?

$$\widehat{R}_+(\phi\hat{\mathbf{n}}) = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \qquad [\widehat{R}_+(\phi\hat{\mathbf{n}})]^{-1} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\widehat{R}^{-1}\mathbf{r} = \widehat{R}^{-1}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}}(x-y) \\ \frac{1}{\sqrt{2}}(x+y) \\ z \end{pmatrix}$$

$$(\widehat{O}_R f)(\mathbf{r}) = f(\widehat{R}^{-1}\mathbf{r}) = f\left(\tfrac{1}{\sqrt{2}}(x-y), \tfrac{1}{\sqrt{2}}(x+y), z\right) = \tfrac{1}{2}(x^2-y^2)\exp\left(-r^2\right)$$



$x\,y\ \exp\left(-r^2\right)\ (d_{xy})$

$\frac{1}{2}(x^2 - y^2)\exp\left(-r^2\right)\ (d_{x^2-y^2})$

Some Continuous Groups (incl. Classical Groups)

Group elements are represented as non-singular (i. e. invertible) $n \times n$ matrices A.
Matrix elements are continuous functions of a set of parameters: $A = A(\alpha_1, \ldots, \alpha_r)$.
Under certain conditions, the resulting groups may qualify as Lie groups.

No.	Symbol[a]	Number r of real parameters	Remarks
1	$GL(n, \mathbb{C})$	$2n^2$	general complex linear group of degree n
2	$GL(n, \mathbb{R})$	n^2	general real linear group of degree n
3	$SL(n, \mathbb{C})$	$2(n^2 - 1)$	special complex linear group of degree n ($\det = +1$)
4	$SL(n, \mathbb{R})$	$n^2 - 1$	special real linear group of degree n ($\det = +1$)
5	$U(n)$	n^2	unitary group of degree n, leaves invariant $\sum_{i=1}^{n} z_i {z_i}^*$ ($z_i \in \mathbb{C}$)
6	$SU(n)$	$n^2 - 1$	special unitary group of degree n ($\det = +1$)
7	$O(n)$	$n(n-1)/2$	(real) orthogonal group of degree n ($\det = \pm 1$)
8	$SO(n)$	$n(n-1)/2$	special orthogonal group of degree n ($\det = +1$), leaves invariant $\sum_{i=1}^{n} {x_i}^2$ ($x_i \in \mathbb{R}$)
9	$Aff(n, \mathbb{R})$	$n^2 + n$	group of invertible affine transformations in $\mathbb{R}^n$: $\mathbf{r}' = A\,\mathbf{r} + \mathbf{a}$ (A nonsingular matrix, $\mathbf{a}$ vector)

[a] adapted from BG Wybourne, *Classical Groups for Physicists*, Wiley, 1974

Examples:

(1) Complex numbers of modulus 1, $U(1)$ ($1^2 = 1$ real parameter):

$$U(1) = \{\exp(i\phi)\,;0 \leq \phi < 2\pi\}$$

(2) 2×2 unitary matrices with $\det = +1$, $SU(2)$ ($2^2 - 1 = 3$ real parameters):

$$SU(2) = \left\{ \begin{pmatrix} a & -b^* \\ b & a^* \end{pmatrix} ; a, b \in \mathbb{C}\,; \det\, = aa^* + bb^* = 1 \right\}$$

$SU(2)$ is the double cover group of $SO(3)$ (group of rotations of a 3D sphere), i. e. there exists a two-to-one homomorphism between $SU(2)$ and $SO(3)$ $\rightsquigarrow$ double groups.

(3) 2×2 orthogonal matrices with $\det = +1$, $SO(2)$ ($2 \cdot 1/2 = 1$ real parameter):

$$SO(2) = \left\{ \begin{pmatrix} \cos(\phi) & \sin(\phi) \\ -\sin(\phi) & \cos(\phi) \end{pmatrix} ; 0 \leq \phi < 2\pi \;\; (\text{or} -\pi \leq \phi < \pi) \right\}$$

(4) 3×3 orthogonal matrices ($3 \cdot 2/2 = 3$ real parameters):

$$SO(3) = \{\widehat{R}_+(\varphi\hat{\mathbf{n}})\}\,, \qquad O(3) = \{\widehat{R}_+(\varphi\hat{\mathbf{n}})\} \cup \{\widehat{R}_-(\varphi\hat{\mathbf{n}})\}$$

$SO(3) \equiv \mathbf{K}$ (rotations of the 3D sphere),
$O(3) \equiv \mathbf{K}_h = \mathbf{K} \times \mathbf{C}_i$ (full symmetry of 3D sphere).

Noether's (first) theorem (1918) [1]:

> *To every continuous symmetry of a physical system belongs a conserved quantity.*

Remark: Actually, the action (or the action functional) of the system is studied, and a variational principle must be applicable.

Examples:

Homogeneity of Time $\rightsquigarrow$ Conservation of Energy

Homogeneity of Space $\rightsquigarrow$ Conservation of Linear Momentum

Isotropy of Space $\rightsquigarrow$ Conservation of Angular Momentum

Invariance of scalar quantities under Lorentz transformations $\rightsquigarrow$ Conservation of charges (electric and other) in particle physics

[1] named after Emmy Noether (1881–1935, German mathematician)

Infinite Discrete Groups

Space groups (symmetry groups containing translations)

Translations introduce new symmetry elements:

- Glide planes (reflection & translation)
- Screw axes (rotation & translation)

Now rotations have to map lattice points onto lattice points

$$\rightsquigarrow \qquad \chi(\widehat{R}_{+}) = 1 + 2\cos(\varphi) \in \mathbb{Z}$$

$\rightsquigarrow$ restriction of order of crystallographic axes n to

$$\begin{aligned}
&2 \quad (\chi = -1,\ \varphi = \pi),\\
&3 \quad (\chi = 0,\ \varphi = 2\pi/3),\\
&4 \quad (\chi = 1,\ \varphi = \pi/2),\\
&6 \quad (\chi = 2,\ \varphi = \pi/3),\\
&1 \quad (\chi = 3,\ \varphi = 0).
\end{aligned}$$

$\rightsquigarrow$ restriction to 32 **crystallographic** point groups

Synoptical table of notation for crystallographic and some other point groups and for some examples of space groups[a]

Schoenflies	Hermann-Mauguin	Schoenflies	Hermann-Mauguin	Schoenflies	Hermann-Mauguin	
					short	full
Point Groups						
$\mathbf{C}_1$	1	$\mathbf{C}_i$	$\bar{1}$	$\mathbf{C}_s$	m	
$\mathbf{C}_2$	2	$\mathbf{C}_{2h}$	$2/m$	$\mathbf{C}_{2v}$	$m\,m\,2$	
$\mathbf{C}_3$	3	$\mathbf{C}_{3h} = \mathbf{S}_3$	$\bar{6} = 3/m$	$\mathbf{C}_{3v}$	$3\,\mathrm{m}$	
$\mathbf{C}_4$	4	$\mathbf{C}_{4h}$	$4/m$	$\mathbf{C}_{4v}$	$4\,m\,m$	
$\mathbf{C}_6$	6	$\mathbf{C}_{6h}$	$6/m$	$\mathbf{C}_{6v}$	$6\,m\,m$	
$\mathbf{S}_4$	$\bar{4}$	$\mathbf{S}_6 = \mathbf{C}_{3i}$	$\bar{3}$	$\mathbf{C}_{\infty v}$	$\infty\,m$	
$\mathbf{D}_2$	$2\,2\,2$	$\mathbf{D}_{2d}$	$\bar{4}\,2\,m$	$\mathbf{D}_{2h}$	$m\,m\,m$	$2/m\,2/m\,2/m$
$\mathbf{D}_3$	$3\,2$	$\mathbf{D}_{3h}$	$\bar{6}\,2\,m$	$\mathbf{D}_{3d}$	$\bar{3}\,m$	$\bar{3}\,2/m$
$\mathbf{D}_4$	$4\,2\,2$	$\mathbf{D}_{4d}$	$\bar{8}\,2\,m$	$\mathbf{D}_{4h}$	$4/m\,m\,m$	$4/m\,2/m\,2/m$
$\mathbf{D}_5$	$5\,2$	$\mathbf{D}_{5h}$	$\overline{10}\,2\,m$	$\mathbf{D}_{5d}$	$\bar{5}\,m$	$\bar{5}\,2/m$
$\mathbf{D}_6$	$6\,2\,2$	$\mathbf{D}_{6d}$	$\overline{12}\,2\,m$	$\mathbf{D}_{6h}$	$6/m\,m\,m$	$6/m\,2/m\,2/m$
				$\mathbf{D}_{\infty h}$	$\infty/m\,m$	$\infty/m\,2/m$
$\mathbf{T}$	$2\,3$	$\mathbf{T}_d$	$\bar{4}\,3\,m$	$\mathbf{T}_h$	$m\,\bar{3}$	$2/m\,\bar{3}$
		$\mathbf{O}$	$4\,3\,2$	$\mathbf{O}_h$	$m\,\bar{3}\,m$	$4/m\,\bar{3}\,2/m$
		$\mathbf{I}$	$2\,3\,5$	$\mathbf{I}_h$	$m\,\bar{3}\,\bar{5}$	$2/m\,\bar{3}\,\bar{5}$
Space Groups						
$\mathbf{C}_1^1$	$P\,1$	$\mathbf{C}_i^1$	$P\,\bar{1}$	$\mathbf{C}_s^1$	$P\,m$	$P\,1\,m\,1$
$\mathbf{C}_2^1$	$P\,2$	$\mathbf{C}_2^2$	$P\,2_1$	$\mathbf{C}_{2h}^5$	$P\,2_1/c$	$P\,1\,2_1/c\,1$
$\mathbf{D}_2^1$	$P\,2\,2\,2$	$\mathbf{C}_{2v}^{12}$	$C\,m\,c\,2_1$	$\mathbf{D}_{2h}^{16}$	$P\,n\,m\,a$	$P\,2_1/n\,2_1/m\,2_1/a$
$\mathbf{C}_{4h}^6$	$I\,4_1/a$	$\mathbf{D}_{2d}^3$	$P\,\bar{4}\,2_1\,m$	$\mathbf{D}_{4h}^9$	$P\,4_2/m\,m\,c$	$P\,4_2/m\,2/m\,2/c$
$\mathbf{C}_{3i}^2$	$R\,\bar{3}$	$\mathbf{C}_{6h}^2$	$P\,6_3/m$	$\mathbf{D}_{6h}^4$	$P\,6_3/m\,m\,c$	$P\,6_3/m\,2/m\,2/c$
$\mathbf{T}_d^2$	$F\,\bar{4}\,3\,m$	$\mathbf{O}^3$	$F\,4\,3\,2$	$\mathbf{O}_h^5$	$F\,m\,\bar{3}\,m$	$F\,4/m\,\bar{3}\,2/m$

[a] adapted from U Müller, *Symmetry Relationships between Crystal Structures*, Oxford, 2013

Space group elements: Seitz operator [1] $\{\widehat{R}|\mathbf{t}\}$

Action of Seitz operator $\{\widehat{R}|\mathbf{t}\}$ on position vector $\mathbf{r}$:

$$\mathbf{r}' = \widehat{R}\mathbf{r} + \mathbf{t} \equiv \{\widehat{R}|\mathbf{t}\}\mathbf{r}$$

Closure:

$$\{\widehat{S}|\mathbf{u}\}\{\widehat{R}|\mathbf{t}\}\mathbf{r} = \{\widehat{S}\widehat{R}|\widehat{S}\mathbf{t} + \mathbf{u}\}\mathbf{r}$$

Identity:

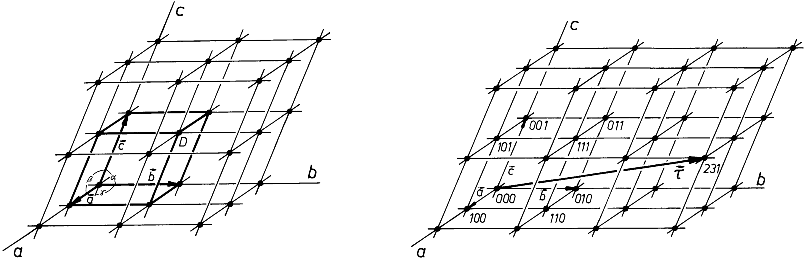
$$\{\widehat{E}|\mathbf{0}\}\mathbf{r} = \mathbf{r}$$

Inverse:

$$\{\widehat{R}|\mathbf{t}\}^{-1}\{\widehat{R}|\mathbf{t}\}\mathbf{r} = \mathbf{r} \qquad \Rightarrow \qquad \{\widehat{R}|\mathbf{t}\}^{-1} = \{\widehat{R}^{-1}| - \widehat{R}^{-1}\mathbf{t}\}$$

[1] named after Frederick Seitz (1911–2008, American physicist)

Lattice in Direct Space (Position Space)



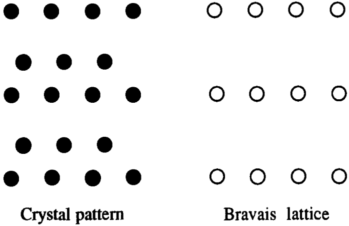
W Borchardt-Ott, Kristallographie, 7. Aufl., Springer, Berlin, 2009

Vectors **of** the direct lattice (lattice translation vectors):
$\mathbf{t}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$ $(u, v, w \in \mathbb{Z})$

Vectors **in** the direct lattice: $\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$ $(x, y, z \in \mathbb{R})$

If $0 \leq x < 1$, $0 \leq y < 1$, $0 \leq z < 1$, then $\mathbf{r}$ belongs to unit cell 000.

Crystal Structure = Lattice + Basis



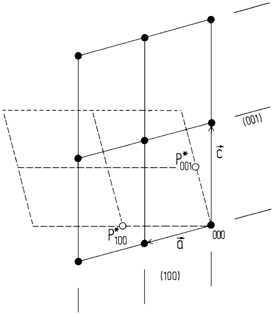
SL Altmann, Band Theory of Solids – An Introduction from the Point of View of Symmetry, Clarendon, Oxford, 1994

The pure translations $\mathcal{T} = \{\{\widehat{E}|\mathbf{t}_{uvw}\}\}$ constitute an Abelian subgroup of the full space group $\mathcal{G}$ of the crystal: $\mathcal{T} \subset \mathcal{G}$

Hence, $\mathcal{T}$ has only one-dimensional IR, their labels $\mathbf{k}$ can be used to label symmetry-adapted crystal orbitals, the so-called Bloch functions [1] $\psi_{j\mathbf{k}}(\mathbf{r})$ (Born–von-Kármán boundary conditions assumed, see below for more on this)

[1] named after Felix Bloch (1905–1983, Swiss-American physicist)

Lattice in Reciprocal Space (Momentum Space)



Introduce a new basis – the basis for reciprocal space – to describe normal vectors of stacks of lattice planes of the direct lattice, such that

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

◀ Example: *ac* plane in a monoclinic primitive lattice

W Borchardt-Ott, Kristallographie, 7. Aufl., Springer, Berlin, 2009

Vectors **of** the reciprocal lattice: $\mathbf{g}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ (Miller indices $h, k, l \in \mathbb{Z}$)

Vectors **in** the reciprocal lattice: $\mathbf{k} = o\mathbf{b}_1 + p\mathbf{b}_2 + q\mathbf{b}_3$ ($o, p, q \in \mathbb{R}$)

	$\mathbf{a}_1$	$\mathbf{a}_2$
Oblique, p	$(a, 0)$	$(b\cos\varphi, b\sin\varphi)$
Rectangular, p	$(a, 0)$	$(0, b)$
Rectangular, c	$(\frac{1}{2}a, \frac{1}{2}b)$	$(-\frac{1}{2}a, \frac{1}{2}b)$
Square, p	$(a, 0)$	$(0, a)$
Hexagonal, p	$(0, -a)$	$(\frac{1}{2}\sqrt{3}a, \frac{1}{2}a)$

	$\mathbf{b}_1$	$\mathbf{b}_2$
Oblique, p	$(2\pi/a)(1, -\cot\varphi)$	$(2\pi/b)(0, \csc\varphi)$
Rectangular, p	$(2\pi/a)(1, 0)$	$(2\pi/b)(0, 1)$
Rectangular, c	$2\pi(1/a, 1/b)$	$2\pi(-1/a, 1/b)$
Square, p	$(2\pi/a)(1, 0)$	$(2\pi/a)(0, 1)$
Hexagonal, p	$(2\pi/a)(1/\sqrt{3}, -1)$	$(2\pi/a)(2/\sqrt{3}, 0)$

Table 3: Basis vectors for the 2D Bravais lattices[a] (top) and the 2D reciprocal lattices[b] (bottom) [1].

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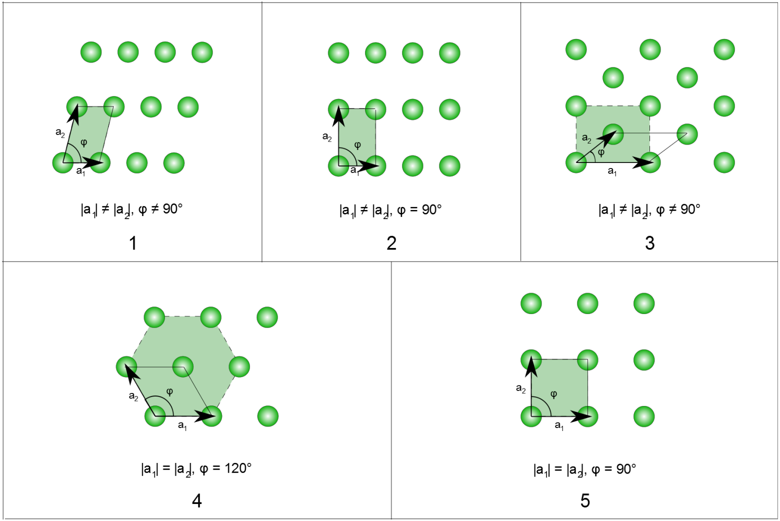
[1] AP Cracknell, *Thin Film Solids* **21** (1974) 107

[a] The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are given in terms of unit vectors in the orthogonal x and y directions

[b] The vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are given in terms of unit vectors in the orthogonal k_x and k_y directions

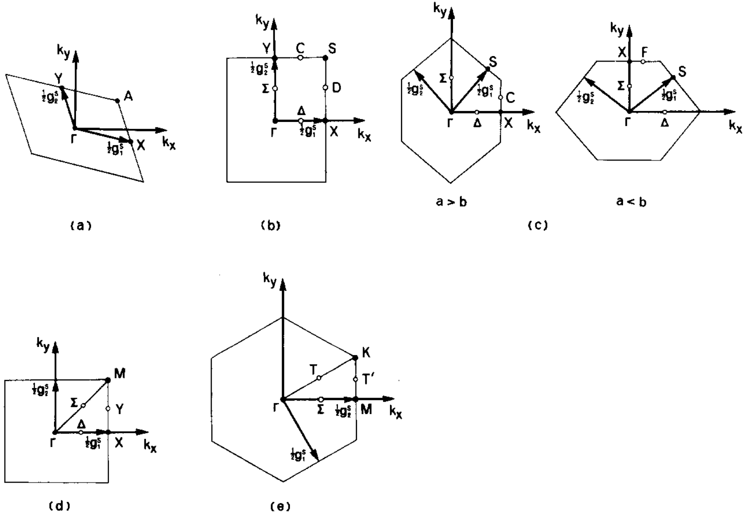
The 2D Bravais Lattices [1]



[1] named after Auguste Bravais (1811–1863, French physicist)

Source of figure: https://en.wikipedia.org/wiki/Bravais_lattice (not fully consistent with table on previous page)

The 2D Reciprocal Lattices



AP Cracknell, *Thin Film Solids* **21** (1974) 107, Fig. 1 (read $\mathbf{g}_i^s$ as $\mathbf{b}_i$)
(a) oblique, p; (b) rectangular, p; (c) rectangular, c; (d) square, p; (e) hexagonal, p

System	No.	Short Symbol	Full Symbol	Generators (in addition to those of $\mathcal{T}$)	Remark••
Oblique	1	p1	p1	$\{\widehat{E}\|\mathbf{0}\}$	s
	2	p2	p211	$\{\widehat{C}_{2z}\|\mathbf{0}\}$	s
Rectangular	3	pm	(p11m)•	$\{\widehat{\sigma}_y\|\mathbf{0}\}$	s
	4	pg	(p11g)•	$\{\widehat{\sigma}_y\|\frac{1}{2}\mathbf{a}_1\}$	ns
	5	cm	c1m1	$\{\widehat{\sigma}_x\|\mathbf{0}\}$	s
	6	pmm	p2mm	$\{\widehat{C}_{2z}\|\mathbf{0}\}$, $\{\widehat{\sigma}_y\|\mathbf{0}\}$	s
	7	pmg	p2mg	$\{\widehat{C}_{2z}\|\mathbf{0}\}$, $\{\widehat{\sigma}_y\|\frac{1}{2}\mathbf{a}_1\}$	ns
	8	pgg	p2gg	$\{\widehat{C}_{2z}\|\mathbf{0}\}$, $\{\widehat{\sigma}_y\|\frac{1}{2}\mathbf{a}_1+\frac{1}{2}\mathbf{a}_2\}$	ns
	9	cmm	c2mm	$\{\widehat{C}_{2z}\|\mathbf{0}\}$, $\{\widehat{\sigma}_x\|\mathbf{0}\}$	s
Square	10	p4	p4	$\{\widehat{C}_{4z}\|\mathbf{0}\}$	s
	11	p4m	p4mm	$\{\widehat{C}_{4z}\|\mathbf{0}\}$, $\{\widehat{\sigma}_x\|\mathbf{0}\}$	s
	12	p4g	p4gm	$\{\widehat{C}_{4z}\|\mathbf{0}\}$, $\{\widehat{\sigma}_y\|\frac{1}{2}\mathbf{a}_1+\frac{1}{2}\mathbf{a}_2\}$	ns
Hexagonal	13	p3	p3	$\{\widehat{C}_3\|\mathbf{0}\}$	s
	14	p3m1	p3m1	$\{\widehat{C}_3\|\mathbf{0}\}$, $\{\widehat{\sigma}_{v1}\|\mathbf{0}\}$	s
	15	p31m	p31m	$\{\widehat{C}_3\|\mathbf{0}\}$, $\{\widehat{\sigma}_{d1}\|\mathbf{0}\}$	s
	16	p6	p6	$\{\widehat{C}_6\|\mathbf{0}\}$	s
	17	p6m	p6mm	$\{\widehat{C}_6\|\mathbf{0}\}$, $\{\widehat{\sigma}_{d1}\|\mathbf{0}\}$	s

Table 4: The 17 two-dimensional space groups [1].

[1] AP Cracknell, *Thin Film Solids* **21** (1974) 107

• Non-standard orientation for groups no. 3 and 4 (compared to the *International Tables*).

•• The symbols s and ns indicate whether the space group is symmorphic or non-symmorphic, respectively.

Space groups (symmetry groups containing translations) ...

- ... with periodicity in **one** dimension:
  2 **line** groups
  (p1: $\cdots \triangleright \triangleright \triangleright \triangleright \triangleright \triangleright \cdots$; p1m: $\cdots \triangleleft \triangleright \triangleleft \triangleright \triangleleft \triangleright \cdots$)
  7 **frieze** groups [1]
  (p1, p1m1, p11m, p11g, p2, p2mm, p2mg)
  75 **rod** groups (if restriction $n \in \{1, 2, 3, 4, 6\}$ is applied)
- ... with periodicity in **two** dimensions:
  17 **plane** groups (wallpaper groups) [2]
  (p1, p1m1, p1g1, c1m1, p211, p2mm, p2mg, p2gg,
  c2mm, p4, p4mm, p4gm, p3, p3m1, p31m, p6, p6mm)
  80 **layer** groups
- ... with periodicity in **three** dimensions:
  230 **space** groups (ES Fedorov, A Schoenflies, 1891/1892)

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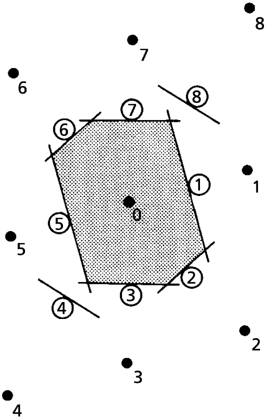
[1] see Hargittay I, Lengyel G, *J. Chem. Educ.* **61** (1984) 1033 for illustrations with Hungarian needlework
[2] see Hargittay I, Lengyel G, *J. Chem. Educ.* **62** (1985) 35 for illustrations with Hungarian needlework

Primitive Domains



Construction of the Voronoi polyhedron (or Dirichlet region) for lattice point **0** leads to ...

... the Wigner-Seitz cell (WS, in direct space)

... the first Brillouin zone (BZ, in reciprocal space)

Knowledge of a periodic function, like

$$f(\mathbf{r}+\mathbf{t}) = f(\mathbf{r}) = \sum_{\mathrm{g}} f_{\mathrm{g}} \frac{1}{\sqrt{V}} \mathrm{e}^{\mathbf{igr}},$$

within the primitive domain is completely sufficient.

C Hammond, The Basics of Crystallography and Diffraction, 3rd ed., Oxford, 2009

Orbitals in Periodic Systems

- Born–von-Kármán boundary conditions: $f(\mathbf{r}+N\mathbf{a}_i)=f(\mathbf{r})$
  $\Rightarrow$ infinite translation subgroup $\mathcal{T}$ replaced by a cyclic group.
- Bloch functions: One-particle functions (crystal orbitals) $\psi_{j\mathbf{k}}(\mathbf{r})$ (j band index; $\mathbf{k}$ IR label within first BZ) of the form

$$\psi_{j\mathbf{k}}(\mathbf{r})=\mathrm{e}^{\mathbf{ikr}}u_{j\mathbf{k}}(\mathbf{r})\,,\quad u_{j\mathbf{k}}(\mathbf{r}+\mathbf{t})=u_{j\mathbf{k}}(\mathbf{r})\,,\quad \psi_{j\mathbf{k}}(\mathbf{r}+\mathbf{t})=\mathrm{e}^{\mathbf{ikt}}\psi_{j\mathbf{k}}(\mathbf{r})\,,$$

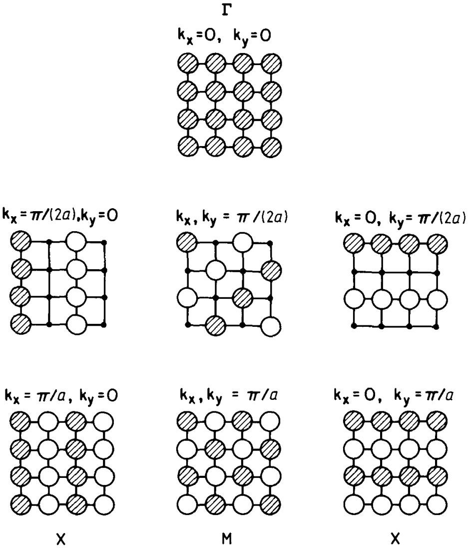
  are plane waves in the lattice, $\mathrm{e}^{\mathbf{ikr}}$, modulated by the periodic cell function $u_{j\mathbf{k}}(\mathbf{r})$.
- Wannier functions: Obtained via unitary transformation of Bloch functions, for example for band j (summation over all N values of $\mathbf{k}$ in the first BZ):

$$\varphi_{j\mathbf{t}}(\mathbf{r})=N^{-1/2}\sum_{\mathbf{k}}\psi_{j\mathbf{k}}(\mathbf{r})\mathrm{e}^{-\mathbf{ikt}}=N^{-1/2}\sum_{\mathbf{k}}u_{j\mathbf{k}}(\mathbf{r})\mathrm{e}^{\mathbf{ik(r-t)}}$$

  Wannier function for 1D free particle (at ‘cell’ 0)

$$\varphi_0(x)=\sqrt{\frac{1}{L}}\frac{\sin\left(\pi x/L\right)}{\pi x/L}\sim x^{-1}$$

Example: Bloch Functions in a Square Lattice



R Hoffmann, Solids and Surfaces, VCH, New York, 1988

Basis Set Expansion of Bloch Functions

- Plane waves (PW)

$$\psi_{j\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{g}} c_{j\mathbf{k},\mathbf{g}} \mathrm{e}^{\mathrm{i}(\mathbf{k}+\mathbf{g})\mathbf{r}} = \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{r}} \sum_{\mathbf{g}} c_{j\mathbf{k},\mathbf{g}} \mathrm{e}^{\mathrm{i}\mathbf{g}\mathbf{r}}$$

  Universal, orthonormal, complete (in principle), basis adapts itself to lattice changes, but practically it always requires pseudopotentials (even for H) and cutoffs at both low and high energy (i. e., magnitude of **k**)

- Localized functions $\chi_\mu(\mathbf{r})$ containing $\exp\left(-\alpha r^2\right)$ (spherical/Cartesian/Hermite Gauss-type functions, GTFs)

$$\psi_{j\mathbf{k}}(\mathbf{r}) = \sum_{m} c_{j\mathbf{k},m} \phi_{m\mathbf{k}}(\mathbf{r}) \,, \quad \phi_{m\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{s}} \varphi_m(\mathbf{r}-\mathbf{s}) \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{s}} \,,$$

$$\varphi_m(\mathbf{r}-\mathbf{s}) = \sum_{\mu} c_\mu^m \chi_\mu(\mathbf{r}-\mathbf{s})$$

  Very compact, hence efficient representation of electronic structure, but this type of basis is incomplete, valence shell exponents need be chosen with care to avoid linear dependence, general systematic way of basis set improvement is still not known

A thought experiment on H_2 and sc-H

Variation of internuclear distance R within a minimal-basis-set description: $\psi(\mathbf{r}) = N \exp(-\zeta r)$ $(r = |\mathbf{r}|)$ at each nucleus

$R/R_e = 0$		$R/R_e = 1 = R_e/R$		$R_e/R = 0$
He $\zeta_{opt} = 2 - 5/16$	←	H_2 $2 > \zeta_{opt} > 1$	←	2 H $\zeta_{opt} = 1$
■ $\zeta_{opt} = +\infty$	←	sc-H $\zeta_{opt} > 1$	←	∞ H $\zeta_{opt} = 1$

Is there a bifurcation point? What about basis set completeness in the periodic case? How to improve basis sets for periodic calculations systematically?

Note: Improvement of the minimal-basis-set description (only s-function) of sc-H crystal requires g-functions ($l = 4$) for $\mathbf{k} = \mathbf{0}$ (Γ point), see FE Harris et al, *Int J Quantum Chem Symp* **5** (1971) 527

A particle in a one-dimensional box

Hamiltonian: $\widehat{H} = -\hbar^2/(2m)\ (\mathrm{d}/\mathrm{d}x)^2$, with $0 \leq x \leq L$.
Boundary conditions: $\psi(0) = \psi(L) = 0$.
Eigenfunctions and eigenvalues ($n = 1, 2, 3, \ldots$):

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(k_n x\right), \qquad k_n = \frac{n\pi}{L}, \qquad E_n = \frac{(\hbar k_n)^2}{2m} = \frac{h^2}{8mL^2}\,n^2\,.$$

Use of the orthonormal set $\{\psi_n\}$ for Fourier series expansions, e. g.:

$$\phi(x) = \sqrt{\frac{30}{L}}\frac{x}{L}\left(1 - \frac{x}{L}\right) = \sum_{n=1}^{\infty} b_n \psi_n(x)\,, \qquad \langle E\rangle = \frac{h^2}{8mL^2}\frac{10}{\pi^2} > E_1\,,$$

$$b_n = \langle\psi_n|\phi\rangle = \int_0^L \psi_n(x)\phi(x)\,\mathrm{d}x = \frac{4\sqrt{15}}{(n\pi)^3}(1 - (-1)^n) \sim n^{-3}\,.$$

Probability to detect ground-state energy E_1 in a measurement:

$$w_1 = |b_1|^2 = \frac{960}{\pi^6} \approx 0.9986\,.$$

The periodic situation

Primitive period: L.
Periodic functions: $\phi(x+L)=\phi(x)$.
Definition of $\phi(x)$ over interval of length L is sufficient: $0 \le x < L$.

The Fourier series expansion technique now requires an extended (modified) orthonormal basis set ($n=1,2,3,\ldots$):

$$\left\{\sqrt{\frac{1}{L}},\ \chi_n(x)=\sqrt{\frac{2}{L}}\cos\left(k_n x\right),\ \psi_n(x)=\sqrt{\frac{2}{L}}\sin\left(k_n x\right)\right\},\ k_n=\frac{2n\pi}{L}\,.$$

Two simple cases:

- $\phi(0)=\phi(L)=0$, $\phi'(0)=\phi'(L)>0$, e. g.:

$$\phi(x)=N\,\frac{x}{L}\left(\frac{x}{L}-\frac{1}{2}\right)\left(\frac{x}{L}-1\right)=\sum_{n=1}^{\infty} b_n\psi_n(x)\,,\quad b_n\sim n^{-3}\,.$$

- $\phi(0)=\phi(L)>0$, $\phi'(0)=\phi'(L)=0$, e. g.:

$$\phi(x)=N\left(\frac{1}{32}-\left(\frac{x}{L}\right)^2\left(\frac{x}{L}-1\right)^2\right)=\frac{a_0}{\sqrt{L}}+\sum_{n=1}^{\infty} a_n\chi_n(x)\,,\quad a_n\sim n^{-4}\,.$$

The periodic situation (contd)

Alternatively, Fourier series expansion in terms of complex-valued basis ($k_n = 2n\pi/L$):

$$\psi(x) = \frac{a_0}{\sqrt{L}} + \sum_{n=1}^{\infty} \left\{ a_n \sqrt{\frac{2}{L}} \cos(k_n x) + b_n \sqrt{\frac{2}{L}} \sin(k_n x) \right\}$$

$$= \sum_{n=-\infty}^{\infty} c_n \frac{1}{\sqrt{L}} \exp(\mathrm{i} k_n x)$$

$$a_0 = c_0\,, \quad a_n = (c_n + c_{-n})/2\,, \quad b_n = (c_n - c_{-n})/(2\mathrm{i})\,.$$

Fourier series expansion in 3D:

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} \frac{1}{\sqrt{V}} \exp(\mathrm{i}\mathbf{k}\mathbf{r})$$

i. e., superposition of plane waves (**k** direction of propagation)

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