Symmetry I - Crystals and Atoms

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WFS-2025 - Wave function methods for solid state matter
Gdańsk, March 2025

Table of Contents

Table of Contents

Symmetry and quantum mechanics

Groups and representations

- All symmetry operations g_i (e.g. rotations, reflections, ...) and their "multiplication" $\circ$ form a group (G):
  - Closure: $g_i \circ g_j \in G$.
  - Associativity: $(g_i \circ g_j) \circ g_k = g_i \circ (g_j \circ g_k)$.
  - Unity element: $g_i \circ E = E \circ g_i = g_i$.
  - Inverse element: $g_i \circ g_i^{-1} = g_i^{-1} \circ g_i = E$.
- Effect on state vector in Hilbert space: $|\Psi'\rangle = U(g_i)\,|\Psi\rangle$
- Expand in basis: matrix representation

$$U(g_i)\,|\psi_n\rangle = \sum_m [\Gamma(g_i)]_{mn}\,|\psi_m\rangle$$

Symmetry and quantum mechanics

Groups and representations

- Reducible representation:

$$\Gamma' = S^{-1}\Gamma S = \begin{pmatrix} \Gamma_1 & \mathbf{0} & \cdots \\ \mathbf{0} & \Gamma_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} = \Gamma_1 \oplus \Gamma_2 \oplus \ldots$$

- Direct (or Kronecker) product of representations:

$$\begin{aligned} U(g_i)(\,|\psi_n^{(1)}\rangle\,|\psi_k^{(2)}\rangle) &= \left(\sum_m [\Gamma_1(g_i)]_{mn}\,|\psi_m^{(1)}\rangle\right)\left(\sum_l [\Gamma_2(g_i)]_{lk}\,|\psi_l^{(2)}\rangle\right) \\ &= \sum_{ml} [\Gamma(g_i)]_{ml,\;nk}\,|\psi_m^{(1)}\rangle\,|\psi_l^{(2)}\rangle \end{aligned}$$

Shorthand notation:

$$\Gamma_{ml,\;nk} = (\Gamma_1 \otimes \Gamma_2)_{ml,\;nk} = \Gamma_{1,\;mn}\,\Gamma_{2,\;lk}$$

Symmetry and quantum mechanics

Groups and representations

- Physical observable: $\mathcal{A}\,|\psi_n\rangle = a_n\,|\psi_n\rangle$
- If $\mathcal{A}$ is invariant for G:

$$[\mathcal{A}, U(g_i)] = \mathcal{A}U(g_i) - U(g_i)\mathcal{A} = 0$$

then

$$\mathcal{A}U(g_i)\,|\psi_n\rangle = a_n U(g_i)\,|\psi_n\rangle$$

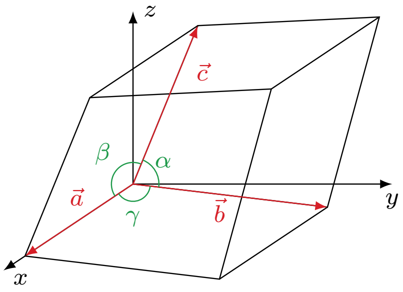
- Eigenstates of an operator can be labeled by representations of symmetry group

Table of Contents

Terminology

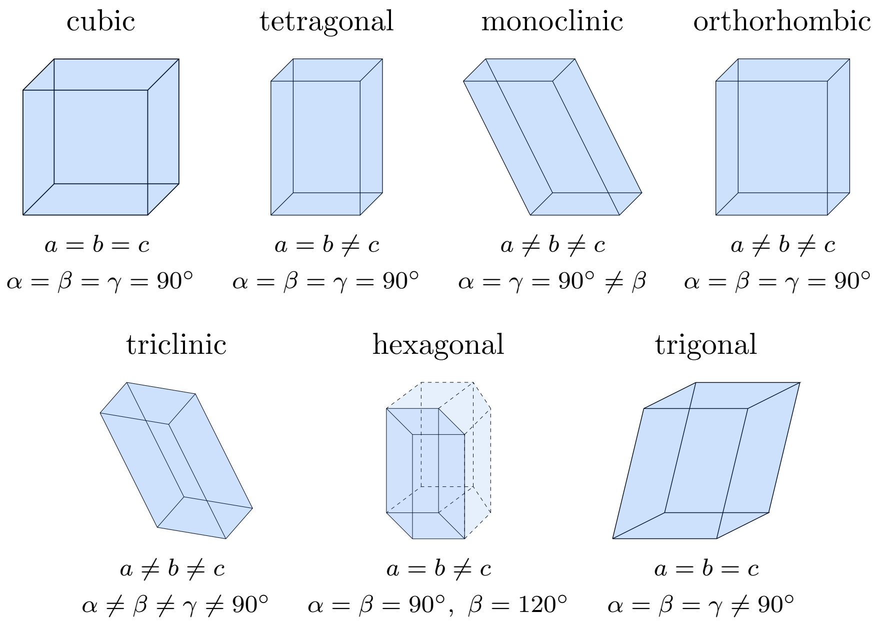
Unit cell

- Crystal: infinite nD periodic array ($n = 3$ in the following)
- Symmetry translations: lattice vectors
- Crystallographic (**affine**) basis: $\vec{a}$, $\vec{b}$, $\vec{c}$
- Unit cell: parallelepiped that contains all $\vec{r} = r_1\vec{a} + r_2\vec{b} + r_3\vec{c}$ for which $0 \leq r_1, r_2, r_3 < 1$
- Lattice parameters: a, b, c, α, β, γ



Terminology

Unit cell



cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$

tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90° \neq \beta$

orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

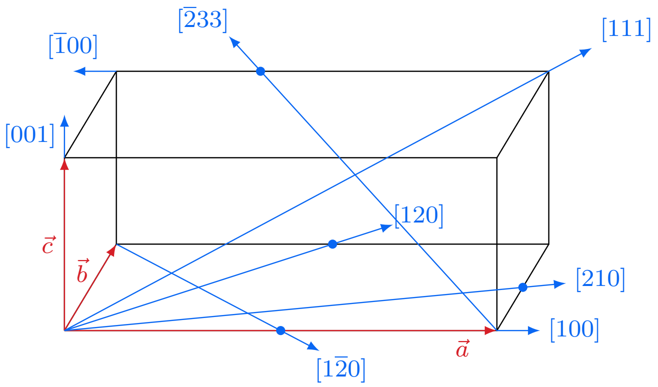
hexagonal
$a = b \neq c$
$\alpha = \beta = 90°,\ \beta = 120°$

trigonal
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

Terminology

Miller indices

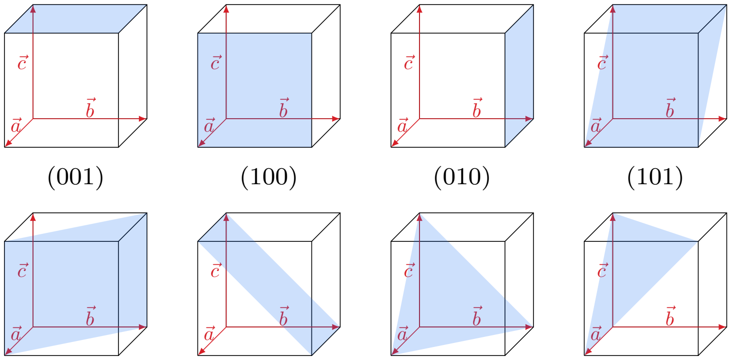
- Direction $[uvw]$: lattice vector $\vec{t} = u\vec{a} + v\vec{b} + w\vec{c}$ with smallest integral u, v, w without common divisor



Terminology

Miller indices

- Direction $[uvw]$: lattice vector $\vec{t} = u\vec{a} + v\vec{b} + w\vec{c}$ with smallest integral u, v, w without common divisor
- Net plane (hkl) (Miller indices): intersects coordinate axes at a/h, b/k, c/l (0 if plane is parallel to axis)
- d_{hkl}: distance between two neighbouring (hkl) planes



(001) (100) (010) (101)

(110) (011) (111) $(1\bar{1}1)$

Crystal coordinates

Metric tensor

- Definition: $g_{ij} = \vec{e}_i \cdot \vec{e}_j$ for a basis e_i
  - Distance between $\vec{u}$ and $\vec{v}$:

$$d_{uv}^2 = g_{ij}(u_i - v_i)(u_j - v_j) = (\vec{u} - \vec{v}) \cdot \boldsymbol{g} \cdot (\vec{u} - \vec{v})$$

  - Angle between $\vec{u}$, $\vec{v}$ and $\vec{w}$ (apex $\vec{v}$):

$$\cos\theta = \frac{1}{d_{uv} d_{vw}}\, g_{ij}(u_i - v_i)(w_j - v_j) = \frac{(\vec{u} - \vec{v}) \cdot \boldsymbol{g} \cdot (\vec{w} - \vec{v})}{d_{uv} d_{vw}}$$

- Examples:
  - Euclidian space $\mathbb{R}^3$, Carthesian basis:

$$\boldsymbol{g} = \mathbb{1}_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

  - Minkowski space $\mathbb{R}^{3,1}$:

$$\boldsymbol{g} = \boldsymbol{\eta} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Crystal coordinates

Metric tensor

Euclidian space $\mathbb{R}^3$, crystallographic bases, $\det(\boldsymbol{g}) = V_{\text{unit cell}}$:

- Cubic:

$$\boldsymbol{g} = \begin{pmatrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & a^2 \end{pmatrix}$$

- Hexagonal:

$$\boldsymbol{g} = \begin{pmatrix} a^2 & -\frac{a^2}{2} & 0 \\ -\frac{a^2}{2} & a^2 & 0 \\ 0 & 0 & c^2 \end{pmatrix}$$

- Trigonal

$$\boldsymbol{g} = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}$$

- Orthorombic:

$$\boldsymbol{g} = \begin{pmatrix} a^2 & 0 & 0 \\ 0 & b^2 & 0 \\ 0 & 0 & c^2 \end{pmatrix}$$

- Monoclinic:

$$\boldsymbol{g} = \begin{pmatrix} a^2 & 0 & ac\cos\beta \\ 0 & b^2 & 0 \\ ac\cos\beta & 0 & c^2 \end{pmatrix}$$

Isometries

Symmetry operations

- Leaves all angles and distances (i.e. $\boldsymbol{g}$) unchanged
  1. Identity:

$$\vec{r}\,' = \mathbb{1}_3\vec{r} = \vec{r} \qquad \text{or} \qquad \begin{pmatrix} r_1' \\ r_2' \\ r_3' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

  2. Translation:

$$\vec{r}\,' = \vec{r} + \vec{T} \qquad \text{or} \qquad \begin{pmatrix} r_1' \\ r_2' \\ r_3' \end{pmatrix} = \begin{pmatrix} r_1 + T_1 \\ r_2 + T_2 \\ r_3 + T_3 \end{pmatrix}$$

  3. Rotation:

$$\vec{r}\,' = R\vec{r} \qquad \text{or} \qquad \begin{pmatrix} r_1' \\ r_2' \\ r_3' \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

with $\det(R) = 1$, i.e. $(R \in SO(3))$ and $\cos\varphi = \frac{1}{2}\left(\text{Tr}(R) - 1\right)$

Isometries

Augmented columns and matrices

- Combine translation $(\vec{w})$ and rotation (W), $(W|\vec{w})$ (*Seitz symbol*):

$$\vec{r}' = W\vec{r} + \vec{w} \qquad \text{or} \qquad \begin{pmatrix} r'_1 \\ r'_2 \\ r'_3 \end{pmatrix} = \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} + \begin{pmatrix} w_1 \\ w_2 \\ w_3 \end{pmatrix}$$

- Shorthand notation:

$$\vec{r} \to \mathbb{r} = \left(\begin{array}{c} r_1 \\ r_2 \\ r_3 \\ \hline 1 \end{array}\right) \qquad \text{and} \qquad (W|\vec{w}) \to \mathbb{W} = \left(\begin{array}{ccc|c} W_{11} & W_{12} & W_{13} & w_1 \\ W_{21} & W_{22} & W_{23} & w_2 \\ W_{31} & W_{32} & W_{33} & w_3 \\ \hline 0 & 0 & 0 & 1 \end{array}\right)$$

- Advantage: use 4x4 matrix algebra
  - Consecutive isometries: $(V|\vec{v}) \circ (W|\vec{w}) \to \mathbb{V} \cdot \mathbb{W}$
  - Inverse isometries: $(W|\vec{w})^{-1} \to \mathbb{W}^{-1}$

Isometries

Symmetry operations (continued))

4. Screw rotation: rotation axis and direction of translation coincide. E.g.,

$$\mathbb{W} = \left(\begin{array}{ccc|c} \cos\varphi & -\sin\varphi & 0 & 0 \\ \sin\varphi & \cos\varphi & 0 & 0 \\ 0 & 0 & 1 & w_3 \\ \hline 0 & 0 & 0 & 1 \end{array}\right)$$

5. Inversion:

$$\vec{r}' = -\mathcal{P}\vec{r} + \vec{w} = -\mathbb{1}_3\vec{r} + \vec{w} = -\vec{r} + \vec{w}$$

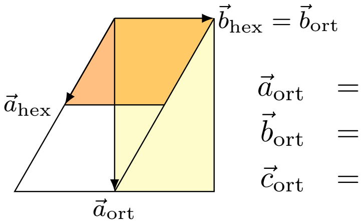
6. Rotoinversion: $(S|\vec{0})$ for which $\det(S) = -1$; $S = \mathcal{P}R = R\mathcal{P}$
7. (Glide) reflections: $(W|\vec{w})$ for which

$$\begin{cases} \det(W) = -1 \\ \mathrm{Tr}(W) = 1 \\ W \neq \mathcal{P} \end{cases}$$

Coordinate transformations

Example 1: From hexagonal to orthorhombic

- Coordinate transformation:



$$\begin{aligned}\vec{a}_{\text{ort}} &= 2\vec{a}_{\text{hex}} + \vec{b}_{\text{hex}}\\ \vec{b}_{\text{ort}} &= \vec{b}_{\text{hex}}\\ \vec{c}_{\text{ort}} &= \vec{c}_{\text{hex}}\end{aligned}$$

$$\begin{aligned}\vec{r}_{\text{ort}} &= \left(\begin{array}{ccc|c} \frac{1}{2} & 0 & 0 & 0\\ -\frac{1}{2} & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ \hline 0 & 0 & 0 & 1\end{array}\right)\vec{r}_{\text{hex}}\\ &= \mathbb{M}\vec{r}_{\text{hex}}\end{aligned}$$

- Transformation of isometry:

$$\mathbb{W}_{\text{hex}} = \left(\begin{array}{ccc|c} 1 & 0 & 0 & 0\\ 1 & -1 & 0 & 0\\ 0 & 0 & 1 & \frac{1}{2}\\ \hline 0 & 0 & 0 & 1\end{array}\right) \qquad \text{(glide reflection)}$$

$$\mathbb{W}_{\text{ort}} = \mathbb{M}\mathbb{W}_{\text{hex}}\mathbb{M}^{-1} = \left(\begin{array}{ccc|c} 1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & 1 & \frac{1}{2}\\ \hline 0 & 0 & 0 & 1\end{array}\right)$$

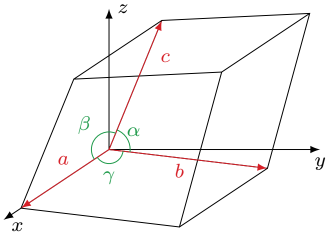
Coordinate transformations

Example 2: From trigonal crystal to Cartesian

- Choice is not unique, e.g.:

$$\vec{a} = \begin{pmatrix} a\\ 0\\ 0\end{pmatrix}, \qquad \vec{b} = \begin{pmatrix} b\cos\gamma\\ b\sin\gamma\\ 0\end{pmatrix},$$

$$\vec{c} = \begin{pmatrix} c\cos\beta\\ c\frac{\cos\alpha - \cos\beta\cos\gamma}{\sin\gamma}\\ c\sqrt{1 - \cos\beta - \left(\frac{\cos\alpha - \cos\beta\cos\gamma}{\sin\gamma}\right)^2}\end{pmatrix}$$



Space groups

Mathematical structure

Space group $\mathcal{G}$: symmetry group of a perfect crystal (all $\mathbb{W} = (W|\vec{w})$): 230 possibilities (Fedorov and Schoenflies, 1891)

- *Translation group* $\mathcal{T} \triangleleft \mathcal{G}$ (i.e. $\mathbb{W}^{-1} \cdot (\mathbb{1}_3|\vec{T}) \cdot \mathbb{W} = (\mathbb{1}_3|\vec{T}')$) = **lattice**
- *Point group of crystal* G = symmetry group of the bundle of the normals on crystal faces: $G = \{W\}$; isomorphic to $\mathcal{G}/\mathcal{T}$ = **crystal class**, 32 possibilities
- *Holohedry of point group* $\mathcal{H}$:
  - Point group of lattice
  - $G \leq \mathcal{H}$
  - index $|\mathcal{H}|/|G|$ as small as possible

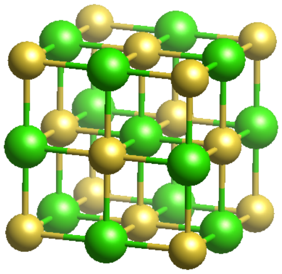
  = **crystal system**: 7 possibilities (triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, cubic)

Space groups

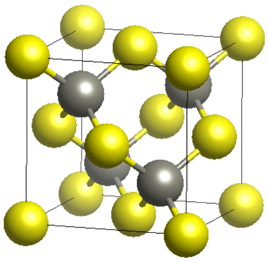
Mathematical structure: point groups

Example: cubic holohedry

- Rocksalt NaCl
  - Holohedral
  - $\mathcal{H} = G = m\bar{3}m \quad (= O_h)$



- Sphalerite ZnS
  - Non-holohedral
  - $\mathcal{H} = m\bar{3}m > G = \bar{4}3m \quad (= T_d)$



Visualization with VESTA, Momma and Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).

Space groups

Mathematical structure: point groups

triclinic	1	C_1
	$\bar{1}$	C_i
monoclinic	2	C_2
	m	C_s
	$2/m$	C_{2h}
orthorhombic	222	D_2
	$mm2$	C_{2v}
	mmm	D_{2h}
tetragonal	4	C_4
	$\bar{4}$	S_4
	$4/m$	C_{4h}
	422	D_4
	$4mm$	C_{4v}
	$\bar{4}2m$	D_{2d}
	$4/mmm$	D_{4h}

trigonal	3	C_3
	$\bar{3}$	C_{3i}
	32	D_3
	$3m$	C_{3v}
	$\bar{3}m$	D_{3d}
hexagonal	6	C_6
	$\bar{6}$	C_{3h}
	$6/m$	C_{6h}
	622	D_6
	$6mm$	C_{6v}
	$\bar{6}m2$	D_{3h}
	$6/mmm$	D_{6h}
cubic	23	T
	$m\bar{3}$	T_h
	432	O
	$\bar{4}3m$	T_d
	$m\bar{3}m$	O_h

Space groups

Mathematical structure: lattices

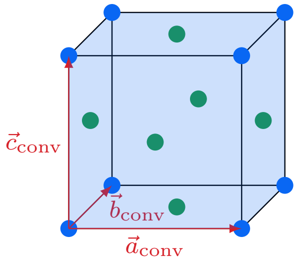
- Bases:
  - Conventional basis: As used by "*International Tables A*" (symmetry-adapted, i.e. user friendliness)
  - Primitive basis: All lattice vectors are *integral* linear combinations of basis vectors
- Lattices:
  - Primitive (P): primitive basis = conventional basis
  - Centered: primitive basis $\neq$ conventional basis
    - Base centered C $(\frac{1}{2}, \frac{1}{2}, 0)$ (or A $(0, \frac{1}{2}, \frac{1}{2})$, B $(\frac{1}{2}, 0, \frac{1}{2})$)
    - Face centered F $(0, \frac{1}{2}, \frac{1}{2},)$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$
    - Body centered I $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
    - Rhombohedral R $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$

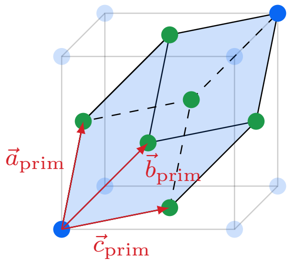
Space groups

Mathematical structure: lattices

Example: FCC, conventional vs. primitive cell

$$\begin{cases} \vec{a}_{\text{prim}} &= \frac{1}{2}\left(\vec{b}_{\text{conv}} + \vec{c}_{\text{conv}}\right) \\ \vec{b}_{\text{prim}} &= \frac{1}{2}\left(\vec{a}_{\text{conv}} + \vec{c}_{\text{conv}}\right) \\ \vec{c}_{\text{prim}} &= \frac{1}{2}\left(\vec{a}_{\text{conv}} + \vec{b}_{\text{conv}}\right) \end{cases}$$





Space groups

Mathematical structure: lattices

- 14 Bravais lattices

name	lattice parameters	centring
cubic primitive (cP)	$a = b = c,\ \alpha = \beta = \gamma = 90°$	
cubic body-centred (cI)	$a = b = c,\ \alpha = \beta = \gamma = 90°$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
cubic face-centred (cF)	$a = b = c,\ \alpha = \beta = \gamma = 90°$	$(0, \frac{1}{2}, \frac{1}{2},),\ (\frac{1}{2}, 0, \frac{1}{2}),\ (\frac{1}{2}, \frac{1}{2}, 0)$
tetragonal primitive (tP)	$a = b \neq c,\ \alpha = \beta = \gamma = 90°$	
tetragonal body-centred (tI)	$a = b \neq c,\ \alpha = \beta = \gamma = 90°$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
orthorhombic primitive (oP)	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$	
orthorhombic body-centred (oI)	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
orthorhombic base-centred (oC)	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$	$(\frac{1}{2}, \frac{1}{2}, 0)$
orthorhombic face-centred (F)	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$	$(0, \frac{1}{2}, \frac{1}{2},),\ (\frac{1}{2}, 0, \frac{1}{2}),\ (\frac{1}{2}, \frac{1}{2}, 0)$
hexagonal primitive (hP)	$a = b \neq c,\ \alpha = \beta = 90°, \gamma = 120°$	
trigonal (rhombohedral) (hR)	$a = b \neq c,\ \alpha = \beta = 90°,\ \gamma = 120°$	$(\frac{2}{3}, \frac{1}{3}, \frac{1}{3}),\ (\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$
rhombohedral (primitive) (rP)	$a = b = c,\ \alpha = \beta = \gamma \neq 90°$	
monoclinic primitive (mP)	$a \neq b \neq c,\ \alpha = \gamma = 90°, \beta \neq 90°$	
monoclinic base-centred (mC)	$a \neq b \neq c,\ \alpha = \gamma = 90°, \beta \neq 90°$	$(\frac{1}{2}, \frac{1}{2}, 0)$
triclinic (aP)	$a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90°$	

Space groups

Hermann–Mauguin notation

- First symbol: Bravais lattice
- Next symbols: Symmetry operations along principal axes:
  - Rotation axes (2, 3, 4, 6)
  - Rotoinversion axes ($\overline{2}$, $\overline{3}$, $\overline{4}$, $\overline{6}$)
  - Mirror planes (m)
  - Screw axes (e.g., 2_1, 3_2, etc.)
  - Glide planes (a, b, c, n, d, e)
- Order of symmetry operation depend on crystal system (e.g. a,b,c for orthorhombic or $\vec{c}$, $\vec{a}$, $\vec{a}-\vec{b}$ for hexagonal)

Space groups

Atomic positions

- Site symmetry group: $G_X \leq G < \mathcal{G}$: leaves X invariant
- Wyckoff positions:
  - Multiplicity: number of symmetry-equivalent positions in unit cell
  - Wyckoff letter (a for highest symmetry)
- Useful website: `https://www.cryst.ehu.es/cryst/get_wp.html`

Space groups

Example

- Chalcopyrite $CuFeS_2$
  - Space group: $F\bar{4}3m$ (№ 216)
  - Crystal class: $\bar{4}3m$ (T_d)
  - Crystal system: Cubic (face-centered - F)

440G Natural Colorful Chalcopyrite Calci Crystal ClustRare Mineral Specim

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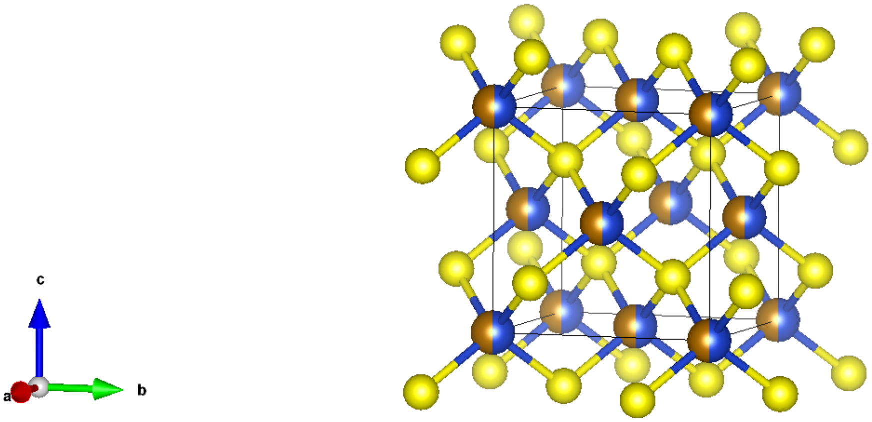
Basics of crystallography

Practical use

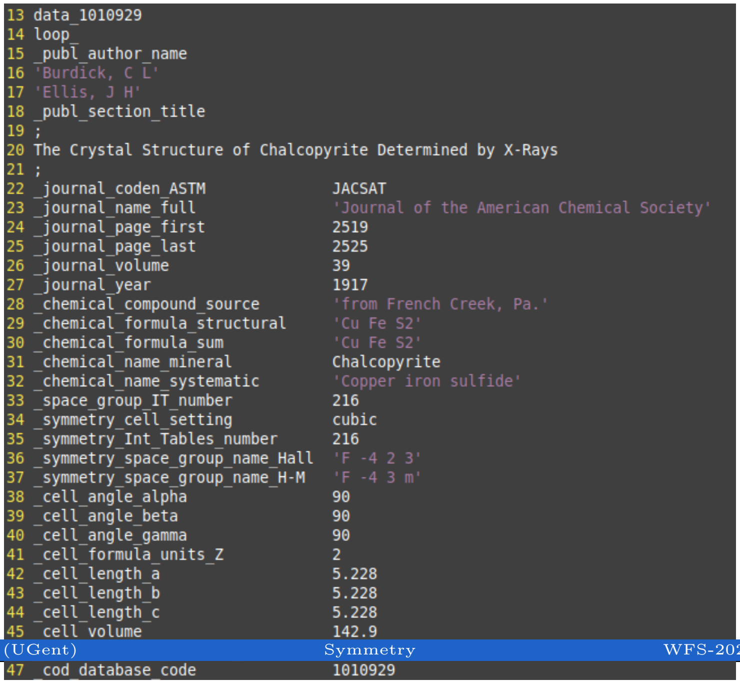


Visualization with VESTA, Momma and Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).

Basics of crystallography

Practical use: Crystallographic Information File (CIF)

- Basic information: reference, name, chemistry, space group, a, b, c, α, β, γ



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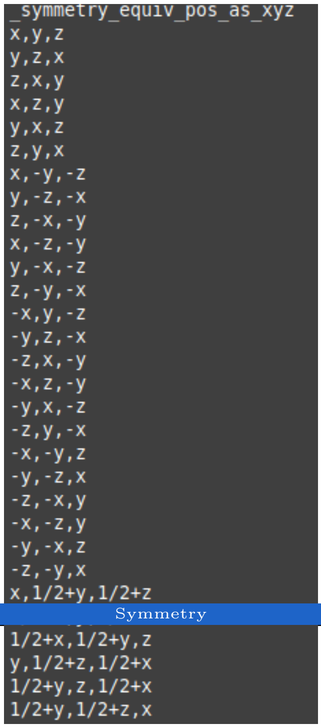
Basics of crystallography

Practical use: Crystallographic Information File (CIF)

- Basic information: reference, name, chemistry, space group, a, b, c, α, β, γ
- Equivalent positions

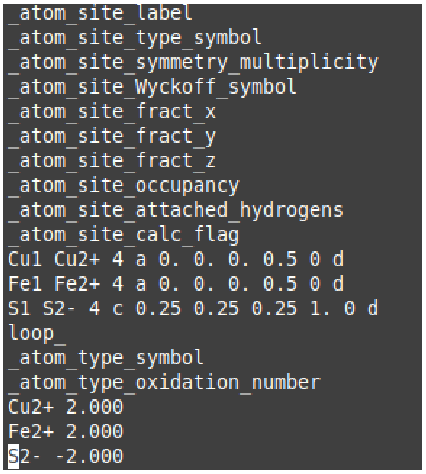


```
_symmetry_equiv_pos_as_xyz
x,y,z
y,z,x
z,x,y
x,z,y
y,x,z
z,y,x
x,-y,-z
y,-z,-x
z,-x,-y
x,-z,-y
y,-x,-z
z,-y,-x
-x,y,-z
-y,z,-x
-z,x,-y
-x,z,-y
-y,x,-z
-z,y,-x
-x,-y,z
-y,-z,x
-z,-x,y
-x,-z,y
-y,-x,z
-z,-y,x
x,1/2+y,1/2+z
1/2+x,1/2+y,z
y,1/2+z,1/2+x
1/2+y,z,1/2+x
1/2+y,1/2+z,x
```

Basics of crystallography

Practical use: Crystallographic Information File (CIF)

- Basic information: reference, name, chemistry, space group, a, b, c, α, β, γ
- Equivalent positions
- Atoms; their charges and positions (fractional coordinates)



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_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_attached_hydrogens
_atom_site_calc_flag
Cu1 Cu2+ 4 a 0. 0. 0. 0.5 0 d
Fe1 Fe2+ 4 a 0. 0. 0. 0.5 0 d
S1 S2- 4 c 0.25 0.25 0.25 1. 0 d
loop_
_atom_type_symbol
_atom_type_oxidation_number
Cu2+ 2.000
Fe2+ 2.000
S2- -2.000
```

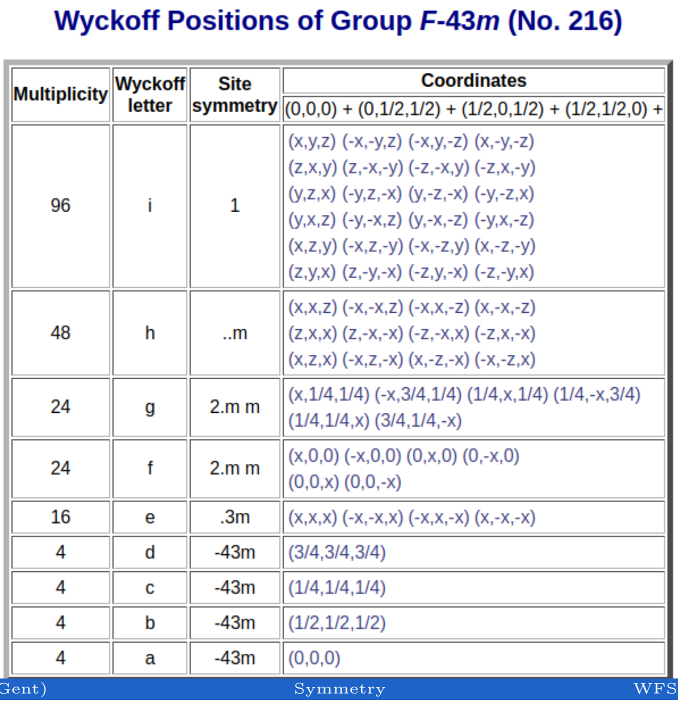
Basics of crystallography

Practical use: Crystallographic Information File (CIF)

- Basic information: reference, name, chemistry, space group, a, b, c, α, β, γ
- Equivalent positions
- Atoms; their charges and positions (fractional coordinates)
- Wyckoff positions (e.g. Cu is on $4a$):
  - Multiplicity (4): number of equivalent positions in unit cell
  - Wyckoff letter (a): alphabetic, ordered with decreasing point symmetry
  - Point group ($\bar{4}3m = T_d$)

Basics of crystallography

Practical use: Crystallographic Information File (CIF)



Wyckoff Positions of Group *F*-43*m* (No. 216)

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
			(0,0,0) + (0,1/2,1/2) + (1/2,0,1/2) + (1/2,1/2,0) +
96	i	1	(x,y,z) (-x,-y,z) (-x,y,-z) (x,-y,-z) (z,x,y) (z,-x,-y) (-z,-x,y) (-z,x,-y) (y,z,x) (-y,z,-x) (y,-z,-x) (-y,-z,x) (y,x,z) (-y,-x,z) (y,-x,-z) (-y,x,-z) (x,z,y) (-x,z,-y) (-x,-z,y) (x,-z,-y) (z,y,x) (z,-y,-x) (-z,y,-x) (-z,-y,x)
48	h	..m	(x,x,z) (-x,-x,z) (-x,x,-z) (x,-x,-z) (z,x,x) (z,-x,-x) (-z,-x,x) (-z,x,-x) (x,z,x) (-x,z,-x) (x,-z,-x) (-x,-z,x)
24	g	2.m m	(x,1/4,1/4) (-x,3/4,1/4) (1/4,x,1/4) (1/4,-x,3/4) (1/4,1/4,x) (3/4,1/4,-x)
24	f	2.m m	(x,0,0) (-x,0,0) (0,x,0) (0,-x,0) (0,0,x) (0,0,-x)
16	e	.3m	(x,x,x) (-x,-x,x) (-x,x,-x) (x,-x,-x)
4	d	-43m	(3/4,3/4,3/4)
4	c	-43m	(1/4,1/4,1/4)
4	b	-43m	(1/2,1/2,1/2)
4	a	-43m	(0,0,0)

Table of Contents

Spherical symmetry

- $O(3)$: orthogonal matrices ($R^T = R^{-1}$) preserve inner product: represent rotations/reflections, $\det R = \pm 1$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

- $SO(3)$: special orthogonal matrices, rotations only, $\det O = 1$
- If R is rotation over angle α along axis $\vec{n}$:

$$U(R) = \exp -\frac{\mathrm{i}}{\hbar}\alpha\left(\hat{\vec{\ell}} \cdot \vec{n}\right),$$

i.e. angular momenta are *generators* for rotations

Spherical symmetry

- Spherically symmetric Hamiltonian:

$$\left[\hat{H}, U(R)\right] = \left[\hat{H}, \hat{\ell}_i\right] = 0 \qquad (i = x, y, z)$$

- IRs of $O(3)$ are labels for energy eigenvalues
- SO(3): integer representations: $\ell = 0$ (s), $\ell = 1$ (p), $\ell = 2$ (d), ...
- SU(2): special unitary matrices ($U^\dagger = U^{-1}$), homomorphic (2:1) with SO(3): also half-integer representations (needed for spin, see further)

Spherical symmetry

- IR ℓ is $(2\ell+1)$-dimensional and basis functions fulfill

$$\begin{aligned}\hat{\ell}^2\,|\ell m_\ell\rangle &= \hbar^2\ell(\ell+1)\,|\ell m_\ell\rangle\\ \hat{\ell}_z\,|\ell m_\ell\rangle &= \hbar m_\ell\,|\ell m_\ell\rangle\end{aligned}$$

- Also useful:

$$\hat{\ell}_\pm\,|\ell m_\ell\rangle = (\hat{\ell}_x \pm \mathrm{i}\hat{\ell}_y)\,|\ell m_\ell\rangle = \hbar\sqrt{\ell(\ell+1)-m_\ell(m_\ell\pm 1)}\,|\ell m_\ell \pm 1\rangle$$

Spherical symmetry

- Wigner-$\mathcal{D}$ matrices:

$$U(R)\,|\ell m_\ell\rangle = \sum_{m'=-\ell}^{\ell}\mathcal{D}^{(\ell)}_{m'm}(R)\,|\ell m_\ell\rangle$$

- Clebsch-Gordan series:

$$\begin{aligned}(\mathcal{D}^{(\ell_1)}\otimes\mathcal{D}^{(\ell_2)})_{m_1m_2,\,m_1'm_2'} &= \mathcal{D}^{(\ell_1)}_{m_{\ell 1}m_{\ell 1'}}(R)\,\mathcal{D}^{(\ell_2)}_{m_{\ell 2}m_{\ell 2'}}(R)\\ &= \sum_{\ell=|\ell_1-\ell_2|}^{\ell_1+\ell_2}\ \sum_{m,m'=-\ell}^{\ell}\langle\ell_1\ell_2m_1m_2\,|\ell_1\ell_2\ell m\rangle\\ &\quad\times\langle\ell_1\ell_2m_1'm_2'\,|\ell_1\ell_2\ell m'\rangle\mathcal{D}^{(\ell)}_{mm'}(R)\end{aligned}$$

shorthand notation:

$$\ell_1\otimes\ell_2 = \bigoplus_{\ell=|\ell_1-\ell_2|}^{\ell_1+\ell_2}\ell$$

Atomic Hamiltonian

$$\boxed{\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2}$$

- Bohr Hamiltonian:

$$\hat{H}_0 = \sum_{i=1}^{N} \left(\frac{-\hbar^2}{2m_e} \hat{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right)$$

- Inter-electronic Coulomb repulsion:

$$\hat{H}_1 = \frac{1}{2} \sum_{i=1}^{N} \sum_{i=j}^{N} \frac{e^2}{4\pi\epsilon_0 \left| \vec{r}_i - \vec{r}_j \right|}$$

- Spin-orbit coupling:

$$\hat{H}_2 = \sum_{i=1}^{N} \xi(r_i) \hat{\vec{\ell}}_i \cdot \hat{\vec{s}}_i$$

Atomic Hamiltonian

Good quantum numbers

$$\boxed{\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2}$$

- Single-electron quantum numbers:
  - ℓ_i, m_{ℓ_i}, s_i, m_{s_i} good quantum numbers for eigenstates of $\hat{H}_0$:

$$\left[\hat{\ell}_i^2, \hat{H}_0\right] = \left[\hat{\ell}_{z_i}, \hat{H}_0\right] = \left[\hat{s}_i^2, \hat{H}_0\right] = \left[\hat{s}_{z_i}, \hat{H}_0\right] = 0$$

  - No good quantum numbers for $\hat{H}_1$ ($\propto 1/r_{ij}$):

$$\left[\hat{\ell}_i^2, \hat{H}_1\right] \neq 0 \quad \text{and} \quad \left[\hat{\ell}_{z_i}, \hat{H}_1\right] \neq 0$$

Atomic Hamiltonian

Good quantum numbers

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2$$

- Single-electron quantum numbers:
  - ℓ_i, m_{ℓ_i}, s_i, m_{s_i} good quantum numbers for eigenstates of $\hat{H}_0$
  - No good quantum numbers for $\hat{H}_1$ ($\propto 1/r_{ij}$)
- Multi-electron quantum numbers:

$$\hat{\vec{L}} = \sum_{i=1}^{N} \hat{\vec{\ell}}_i \qquad \hat{\vec{S}} = \sum_{i=1}^{N} \hat{\vec{s}}_i$$

  - L, M_L good quantum numbers for eigenstates of $\hat{H}_1$:

$$\left[\hat{L}^2, \hat{H}_1\right] = \left[\hat{L}_z, \hat{H}_1\right] = \left[\hat{S}^2, \hat{H}_1\right] = \left[\hat{S}_z, \hat{H}_1\right] = 0$$

Atomic Hamiltonian

Good quantum numbers

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2$$

- Single-electron quantum numbers:
  - ℓ_i, m_{ℓ_i}, s_i, m_{s_i} good quantum numbers for eigenstates of $\hat{H}_0$
  - No good quantum numbers for $\hat{H}_1$ ($\propto 1/r_{ij}$)
- Multi-electron quantum numbers
  - L, M_L good quantum numbers for eigenstates of $\hat{H}_1$:
- Spin-orbit coupling
  - ℓ_i, m_{ℓ_i}, s_i, m_{s_i}, L, M_L, S, M_S no good quantum numbers for $\hat{H}_2$ ($\propto \hat{\vec{L}} \cdot \hat{\vec{S}}$)
  - Further couple momenta:

$$\hat{\vec{j}}_i = \hat{\vec{\ell}}_i + \hat{\vec{s}}_i \qquad \hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$

  - Both single-electron quantum numbers j_i and m_{j_i} as well as multi-electron quantum numbers J and M_J are good:

$$\left[\hat{j}_i^2, \hat{H}_2\right] = \left[\hat{j}_{z_i}, \hat{H}_2\right] = \left[\hat{J}^2, \hat{H}_2\right] = \left[\hat{J}_z, \hat{H}_2\right] = 0$$

Atomic Hamiltonian

Good quantum numbers

$$\boxed{\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2}$$

- Single-electron quantum numbers:
  - ℓ_i, m_{ℓ_i}, s_i, m_{s_i} good quantum numbers for eigenstates of $\hat{H}_0$
  - No good quantum numbers for $\hat{H}_1$ ($\propto 1/r_{ij}$)
- Multi-electron quantum numbers
  - L, M_L good quantum numbers for eigenstates of $\hat{H}_1$:
- Spin-orbit coupling
  - ℓ_i, m_{ℓ_i}, s_i, m_{s_i}, L, M_L, S, M_S no good quantum numbers for $\hat{H}_2$ ($\propto \hat{\vec{L}} \cdot \hat{\vec{S}}$)
  - Both single-electron quantum numbers j_i and m_{j_i} as well as multi-electron quantum numbers J and M_J are good
- Only J and M_J common ground for $\hat{H}_0$, $\hat{H}_1$ and $\hat{H}_2$

Atomic Hamiltonian

$$\boxed{\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2}$$

- Bohr Hamiltonian:

$$\hat{H}_0 = \sum_{i=1}^{N} \left(\frac{-\hbar^2}{2m_e} \hat{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right)$$

- Inter-electronic Coulomb repulsion:

$$\hat{H}_1 = \frac{1}{2} \sum_{i=1}^{N} \sum_{i=j}^{N} \frac{e^2}{4\pi\epsilon_0 \left| \vec{r}_i - \vec{r}_j \right|}$$

- Spin-orbit coupling:

$$\hat{H}_2 = \sum_{i=1}^{N} \xi(r_i) \hat{\vec{\ell}}_i \cdot \hat{\vec{s}}_i$$

Atomic Hamiltonian

Towards approximate solutions with perturbation theory

$$\boxed{\hat{H} = \hat{H}_0' + \hat{H}_1' + \hat{H}_2}$$

- Central field Hamiltonian:

$$\hat{H}_0' = \left(\sum_{i=1}^{N} \frac{-\hbar^2}{2m_e} \hat{\nabla}_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i=1}^{N} V(r_i)$$

- Russell-Saunders Hamiltonian:

$$\hat{H}_1' = \frac{1}{2} \sum_{i=1}^{N} \sum_{i=j}^{N} \frac{e^2}{4\pi\epsilon_0 \left| \vec{r}_i - \vec{r}_j \right|} - \sum_{i=1}^{N} V(r_i)$$

- Spin-orbit coupling:

$$\hat{H}_2 = \sum_{i=1}^{N} \xi(r_i) \hat{\vec{\ell}}_i \cdot \hat{\vec{s}}_i$$

Atomic Hamiltonian

Towards approximate solutions with perturbation theory

- Different choices rationalized from "coupling schemes"

$$\boxed{\hat{H} = \hat{H}_0' + \hat{H}_1' + \hat{H}_2}$$

	term splitting (RS)	multiplet splitting (SO)
$3d$	1-10 eV	0.1 eV
$4d$	1-10 eV	0.1-1 eV
$5d$	1-10 eV	1 eV
$4f$	1-10 eV	0.1-1 eV
$5f$	1-10 eV	1 eV
$5p$	1-10 eV	1 eV
$6p$	1-10 eV	1 eV

Atomic Hamiltonian

Towards approximate solutions with perturbation theory

$$\boxed{\hat{H} = \hat{H}_0' + \hat{H}_1' + \hat{H}_2}$$

- For most atoms $\hat{H}_0' \gg \{\hat{H}_1', \hat{H}_2\}$ holds.
- Perturbation sequence in three steps:

coupling scheme	LS	jj
step 0	$\hat{H}_0'$ $(\ell_i, m_{\ell_i}, s_i, m_{s_i})$	
step 1	$\hat{H}_1'$ (L, M_L, S, M_S)	$\hat{H}_2$ (j_i, m_{j_i})
step 2	$\hat{H}_2$ (J, M_J)	$\hat{H}_1'$ (J, M_J)

Atomic Hamiltonian

Towards approximate solutions with perturbation theory

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step 2	$\hat{H}_2$ (J, M_J)	$\hat{H}_1'$ (J, M_J)

Atomic Hamiltonian

Towards approximate solutions with perturbation theory

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step 2	$\hat{H}_2$ (J, M_J)	$\hat{H}_1'$ (J, M_J)

Multi-electron basis states: LS coupling

Step 0: central field Hamiltonian

$$\hat{H}_0'\Psi = E_0\Psi \quad \text{with} \quad \hat{H}_0' = \sum_{i=1}^{N} \hat{h}_0'(i)$$

- Independent particle model (IPM):

  $$h_0'(i)\psi_i(i) = \epsilon_i\psi_i(i) \quad (\psi_i(i) \text{ orbitals / single} - \text{electron wave functions})$$

- Radial symmetry $(O(3))$:

  $$\psi_{n_i\ell_i m_{l_i} s_i m_{s_i}}(x_i) = R_{n_i\ell_i}(r_i)Y_{\ell_i m_{\ell_i}}(\Omega_i)\chi_{s_i m_{s_i}}(i)$$

- Multi-electron wave function:

  $$\Psi_{\text{centr.field}}(x_1, \ldots, x_N) = \prod_{i=1}^{N} \psi_{n_i\ell_i m_{\ell_i} s_i m_{s_i}}(x_i)$$

- Total energy: $E_{\text{centr.field}} = \sum_{i=1}^{N} \epsilon_{n_i\ell_i m_{\ell_i} s_i m_{s_i}}$

Multi-electron basis states: LS coupling

Step 0: central field Hamiltonian

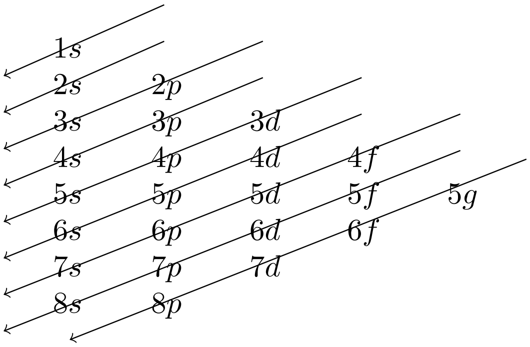
- Independent particle model (IPM)
- Radial symmetry ($O(3)$)
- Multi-electron wave function: Slater determinants
  - Pauli exclusion principle must be respected!

$$\begin{aligned}
\Psi_{\text{centr.field}}(x_1,\ldots,x_N) &= \hat{A}\prod_{i=1}^{N}\psi_{n_i\ell_i m_{\ell_i} s_i m_{s_i}}(x_i)\\
&= \frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & \psi_2(1) & \ldots & \psi_N(1)\\ \psi_1(2) & \psi_2(2) & \ldots & \psi_N(2)\\ \vdots & \vdots & \ldots & \vdots\\ \psi_1(N) & \psi_2(N) & \ldots & \psi_N(N)\end{vmatrix}\\
&= |\psi_1\psi_2\ldots\psi_N|
\end{aligned}$$

Multi-electron basis states: LS coupling

Step 0: central field Hamiltonian

- Independent particle model (IPM)
- Multi-electron wave function: Slater determinants
- Consequence of $\hat{H}_0'$: *aufbau principle*



	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
$n = 1$	$1s$				
$n = 2$	$2s$	$2p$			
$n = 3$	$3s$	$3p$	$3d$		
$n = 4$	$4s$	$4p$	$4d$	$4f$	
$n = 5$	$5s$	$5p$	$5d$	$5f$	$5g$
$n = 6$	$6s$	$6p$	$6d$	$6f$	
$n = 7$	$7s$	$7p$	$7d$		
$n = 8$	$8s$	$8p$			

Multi-electron basis states: *LS* coupling

Step 0: central field Hamiltonian

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

			*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

---

Multi-electron basis states: *LS* coupling

Step 1: Russell-Saunders Hamiltonian

$$\boxed{\hat{H} = \hat{H}_0' + \hat{H}_1' + \hat{H}_2}$$

- For most atoms $\hat{H}_0' \gg \{\hat{H}_1', \hat{H}_2\}$ holds.
- Perturbation sequence in three steps:

coupling scheme	LS	jj
step 0	$\hat{H}_0'$ $(\ell_i, m_{\ell_i}, s_i, m_{s_i})$	
step 1	$\hat{H}_1'$ (L, M_L, S, M_S)	$\hat{H}_2$ (j_i, m_{j_i})
step 2	$\hat{H}_2$ (J, M_J)	$\hat{H}_1'$ (J, M_J)

Multi-electron basis states: LS coupling

Step 1: Russell-Saunders Hamiltonian

- Select a configuration of interest, $n_1\ell_1^{N_1}\dots n_r\ell_r^{N_r}$, with $N_1+\dots+N_r=N$ and degeneracy

$$\prod_{i=1}^{r}\binom{4\ell_i+2}{N_i} \quad = \quad \prod_{i=1}^{r}\frac{(4\ell_i+2)!}{N_i!(4\ell_i+2-N_i)!}$$

- Diagonalization of $\hat{H}_1{}'$ requires basis transformation:

$$\left|{}^{m_{s_1}}_{m_{\ell_1}}\cdots{}^{m_{s_N}}_{m_{\ell_N}}\right| \rightarrow |LM_LSM_S\rangle$$

- Allowed L and S values found by coupling,

$$S = s_1+s_2, s_1+s_2-1, ..., |s_1-s_2|$$

$$L = \ell_1+\ell_2, \ell_1+\ell_2-1, ..., |\ell_1-\ell_2|$$

however within restrictions by Pauli exclusion principle (!)

Multi-electron basis states: LS coupling

Step 2: spin-orbit Hamiltonian

$$\boxed{\hat{H} = \hat{H}_0' + \hat{H}_1' + \hat{H}_2}$$

- For most atoms $\hat{H}_0' \gg \{\hat{H}_1', \hat{H}_2\}$ holds.
- Perturbation sequence in three steps:

coupling scheme	LS	jj
step 0	$\hat{H}_0'\ (\ell_i, m_{\ell_i}, s_i, m_{s_i})$	
step 1	$\hat{H}_1'\ (L, M_L, S, M_S)$	$\hat{H}_2\ (j_i, m_{j_i})$
step 2	$\hat{H}_2\ (J, M_J)$	$\hat{H}_1'\ (J, M_J)$

Multi-electron basis states: LS coupling

Step 2: spin-orbit Hamiltonian

- For every subspace labeled by LS (^{2S+1}L in spectroscopic notation, “term”) of degeneracy $(2S+1)(2L+1)$
- Diagonalization of $\hat{H}_2$ requires another basis transformation:

$$|LM_LSM_S\rangle \rightarrow |LSJM_J\rangle$$

- Allowed J values are straightforwardly found by coupling,

$$J = L+S, L+S-1, ..., |L-S|$$

- Leading to subsubspaces labeled by LSJ ($^{2S+1}L_J$ in spectroscopic notation, “multiplet”) of degeneracy $(2J+1)$

Example: Configurations, terms and multiplets for N

Configurations

- The ground state configuration is readily found from the *aufbau* principle ($Z = 7$).
  - N: [He]$2s^22p^3$

Example: Configurations, terms and multiplets for N

Terms

- Number of Slater determinants: $\frac{6!}{3!3!} = 20$
- Pauli's exclusion principle must be respected: use (M_L, M_S) table:

	2	1	0
$\frac{3}{2}$			$(\overset{+}{1}\overset{+}{0}\text{-}\overset{+}{1})$ ^4S
$\frac{1}{2}$	$(\overset{+}{1}\overset{-}{1}\overset{+}{0})$ ^2D	$(\overset{+}{1}\overset{-}{1}\text{-}\overset{+}{1})$, $(\overset{+}{1}\overset{+}{0}\overset{-}{0})$ ^2D ^2P	$(\overset{+}{1}\overset{+}{0}\text{-}\overset{-}{1})$, $(\overset{+}{1}\overset{-}{0}\text{-}\overset{+}{1})$, $(\overset{-}{1}\overset{+}{0}\text{-}\overset{+}{1})$ ^4S ^2D ^2P

- This means e.g. that

$$\begin{aligned} |p^3(^2D), M_L = 1, M_S = {}^1\!/_2\rangle &= c_1(\overset{+}{1}\overset{-}{1} - \overset{+}{1}) + c_2(\overset{+}{1}\overset{+}{0}\overset{-}{0}) \\ |p^3(^2P),\ M_L = 1, M_S = {}^1\!/_2\rangle &= c_3(\overset{+}{1}\overset{-}{1} - \overset{+}{1}) + c_4(\overset{+}{1}\overset{+}{0}\overset{-}{0}) \end{aligned}$$

i.e. terms are multiconfigurational wave functions

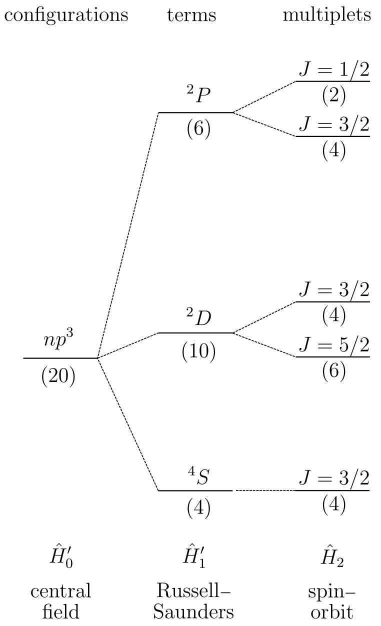
Example: Configurations, terms and multiplets for N

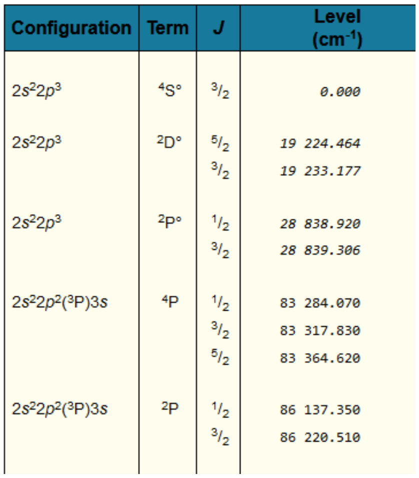
Multiplets

- Angular momentum coupling: $J = |L - S| \ldots L + S$
- ^4S $(L = 0,\ S = {}^3\!/_2)$: $J = {}^3\!/_2$, no splitting
- ^2D $(L = 2,\ S = {}^1\!/_2)$: $J = {}^5\!/_2, {}^3\!/_2$ or $2 \otimes {}^1\!/_2 = {}^5\!/_2 \oplus {}^3\!/_2$
- ^2P $(L = 1,\ S = {}^3\!/_2)$: $J = {}^3\!/_2, {}^1\!/_2$ or $1 \otimes {}^3\!/_2 = {}^3\!/_2 \oplus {}^1\!/_2$

Example: Configurations, terms and multiplets for N

Energy level scheme





Configuration	Term	J	Level (cm^{-1})
$2s^22p^3$	$^4S°$	3/2	0.000
$2s^22p^3$	$^2D°$	5/2	19 224.464
		3/2	19 233.177
$2s^22p^3$	$^2P°$	1/2	28 838.920
		3/2	28 839.306
$2s^22p^2(^3P)3s$	^4P	1/2	83 284.070
		3/2	83 317.830
		5/2	83 364.620
$2s^22p^2(^3P)3s$	^2P	1/2	86 137.350
		3/2	86 220.510

`https://www.nist.gov/pml/atomic-spectra-database`

Literature

Crystal symmetry

INTERNATIONAL TABLES for CRYSTALLOGRAPHY

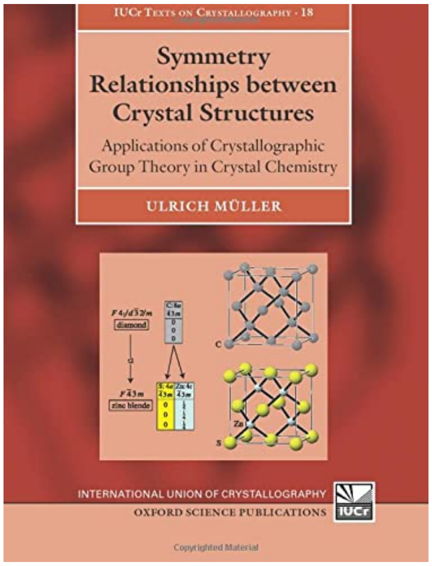
WILEY

Volume A

Space-group symmetry

Edited by Mois I. Aroyo

Sixth edition



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Symmetry Relationships between Crystal Structures

Applications of Crystallographic Group Theory in Crystal Chemistry

ULRICH MÜLLER

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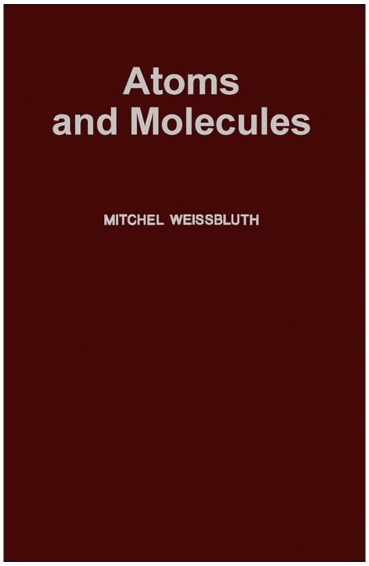
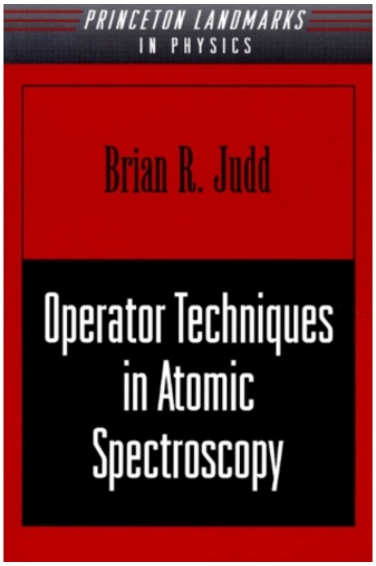
Literature

Atomic symmetry



Atoms
and Molecules

MITCHEL WEISSBLUTH



PRINCETON LANDMARKS
IN PHYSICS

Brian R. Judd

Operator Techniques
in Atomic
Spectroscopy