3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

3.23 Fall 2007 – Lecture 7

ONE BLOCH AT A TIME

Last time

1. Vector space (expectation values measure the projection on different eigenvectors)
2. Eigenvalues and eigenstates as a linear algebra problem
3. Variational principle
4. Its application to a H atom (atomic units)
5. Hamiltonian for a molecular system; bonding and antibonding states
6. Potential energy surface of a molecule
7. Vibrations at equilibrium; quantum harmonic oscillator

Study

- Chapter 2 of Singleton textbook – “Band theory and electronic properties of solids”

Dynamics, Lagrangian style

- First construct *L*=T-V
- Then, the equations of motion are given by

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0$$

(the dot is a time derivative)

- Why ? We can use generalized coordinates. Also, we only need to think at the two scalar functions T and V

Newton's second law, too

- 1-d, 1 particle: $T=1/2\ mv^2$, $V=V(x)$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right)-\frac{\partial L}{\partial q_j}=0$$

$$\frac{d}{dt}\left(\frac{\partial\left(\frac{1}{2}m\dot{x}^2\right)}{\partial \dot{x}}\right)+\frac{\partial V}{\partial x}=0 \quad \Rightarrow \quad \frac{d}{dt}\left(m\dot{x}\right)=-\frac{\partial V}{\partial x}$$

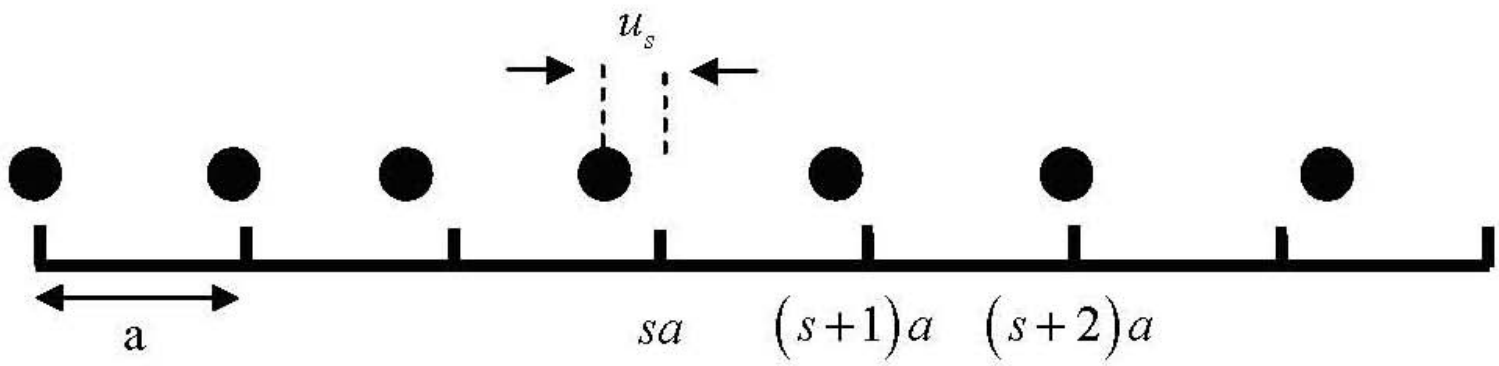
Hamiltonian

- We could use it to derive Hamiltonian dynamics (twice the number of differential equations, but all first order). We introduce a Legendre transformation

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \qquad H(q, p, t) = \sum_i \dot{q}_i p_i - L(q, \dot{q}, t)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad -\dot{p}_i = \frac{\partial H}{\partial q_i}$$

1-dimensional monoatomic chain



Properties

- Unique solutions for k in the first BZ

$$\frac{u_s}{u_{s+1}}$$

- Phase velocity and group velocity

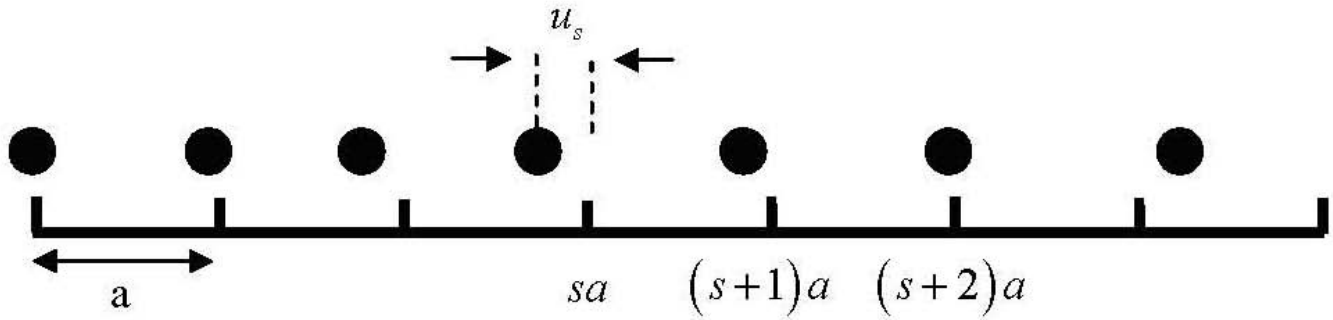
Properties

- Standing waves

- Long wavelength limit

Ring geometry

1-dimensional diatomic chain



III. Equations of motion

$$M\frac{d^2u_{1,s}}{dt^2} = K\left(u_{2,s} - u_{1,s}\right) + G\left(u_{2,s-1} - u_{1,s}\right)$$

$$M\frac{d^2u_{2,s}}{dt^2} = K\left(u_{1,s} - u_{2,s}\right) + G\left(u_{1,s+1} - u_{2,s}\right)$$

IV. Solutions

$$u_{1s} = u_1 e^{iksa}e^{-i\omega t},\ u_{2s} = u_2 e^{iksa}e^{-i\omega t}$$

V. Dispersion relations

$$\left(M\omega^2 - \left(K+G\right)\right)u_1 + \left(K + Ge^{-ika}\right)u_2 = 0$$

$$\left(K + Ge^{ika}\right)u_1 + \left(M\omega^2 - \left(K+G\right)\right)u_2 = 0$$

The homogenous linear equations have a solution only if the determinant of the coefficients is zero:

$$\begin{vmatrix} \left(M\omega^2 - \left(K+G\right)\right) & \left(K+Ge^{-ika}\right) \\ \left(K+Ge^{ika}\right) & \left(M\omega^2 - \left(K+G\right)\right) \end{vmatrix} = 0$$

with solutions:

$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2+G^2+2KG\cos ka}$$

$$\frac{u_1}{u_2} = \mp \frac{K+Ge^{-ika}}{\left|K+Ge^{ika}\right|}$$

for each k there are two solutions which are called the two branches of the dispersion curves.

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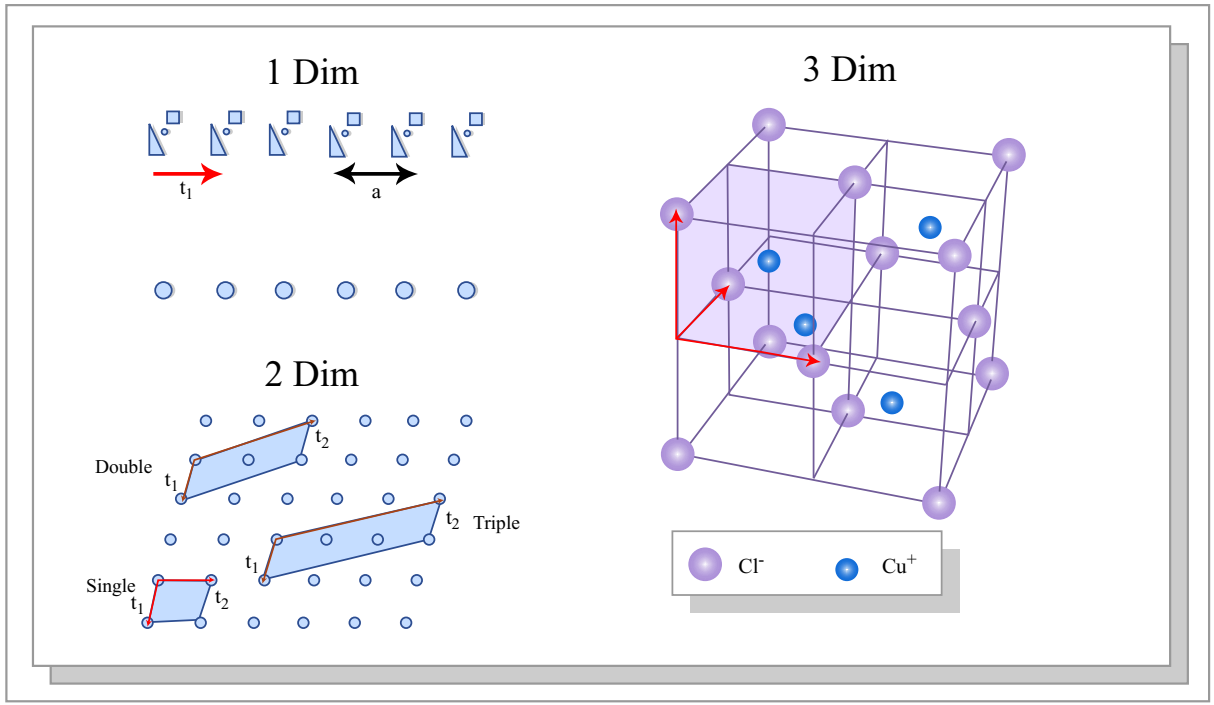
Please see Fig. 22.10 in Ashcroft, Neil W., and N. David Mermin. *Solid State Physics*. Belmont, CA: Brooks/Cole, 1976. ISBN: 9780030839931.

Translational Symmetry



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Bravais Lattices

- Infinite array of points with an arrangement and orientation that appears exactly the same regardless of the point from which the array is viewed.

$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \quad \text{l,m and n integers}$$

$$\vec{a}_1, \vec{a}_2 \text{ and } \vec{a}_3 \text{ primitive lattice vectors}$$

- 14 Bravais lattices exist in 3 dimensions (1848)
- M. L. Frankenheimer in 1842 thought they were 15. So, so naïve…

Bravais lattices

4 Lattice Types

7 Crystal Classes

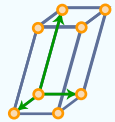
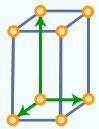
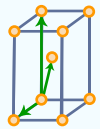
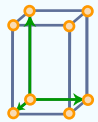
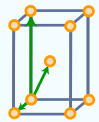
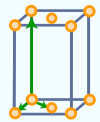
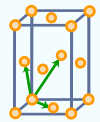
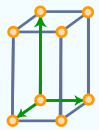
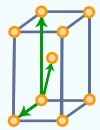
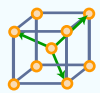
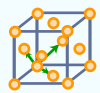
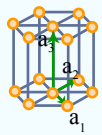
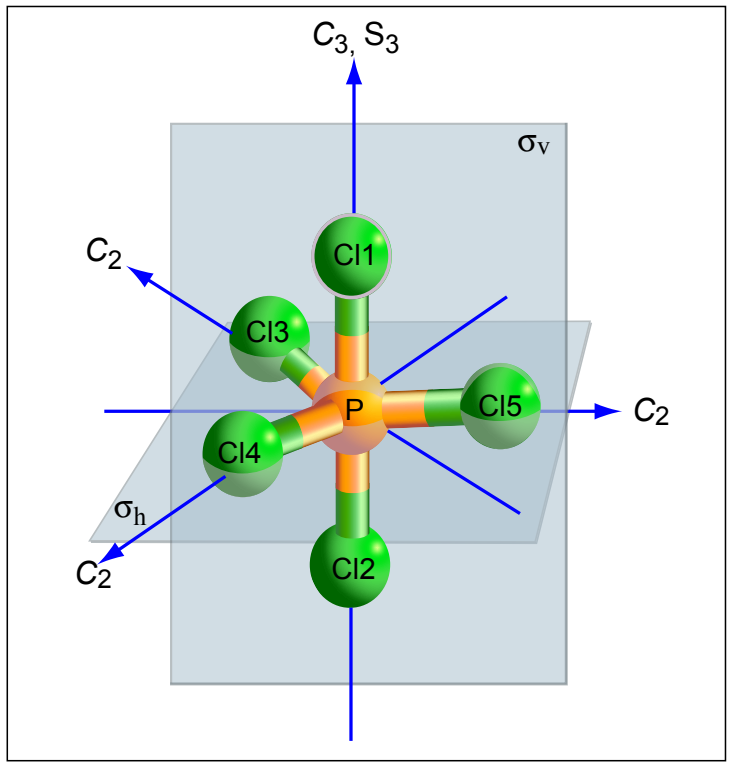
Bravais Lattice	Parameters	Simple (P)	Volume Centered (I)	Base Centered (C)	Face Centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^0$ $\alpha_{12} \neq 90^0$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^0$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^0$ $\alpha_{23} = \alpha_{31} = 90^0$				

Figure by MIT OpenCourseWare.

Symmetry

- Symmetry operations: actions that transform an object into a new but undistinguishable configuration
- Symmetry elements: geometric entities (axes, planes, points…) around which we carry out the symmetry operations

Figure 17.1b



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Symmetry elements and their corresponding operations

Symmetry elements		Symmetry operations	
E	Identity	E	leave molecule unchanged
C_n	n-Fold rotation axis	$\hat{C}_n, \hat{C}_n^2, \ldots, \hat{C}_n^n$	rotate about axis by 360° /n 1, 2, ... , n times (indicated by superscript)
σ	Mirror plane	$\hat{\sigma}$	reflect through the mirror plane
i	Inversion center	$\hat{i}$	(x, y, z)→(-x, -y, -z)
S_n	n-Fold rotation-reflection axis	$\hat{S}_n$	rotate about axis by 360° /n, and reflect through a plane perpendicular to axis.

Group Therapy…

A group G is a finite or infinite set of elements A, B, C, D…together with an operation "☼" that satisfy the four properties of:

1. Closure: If A and B are two elements in G, then A☼B is also in G.

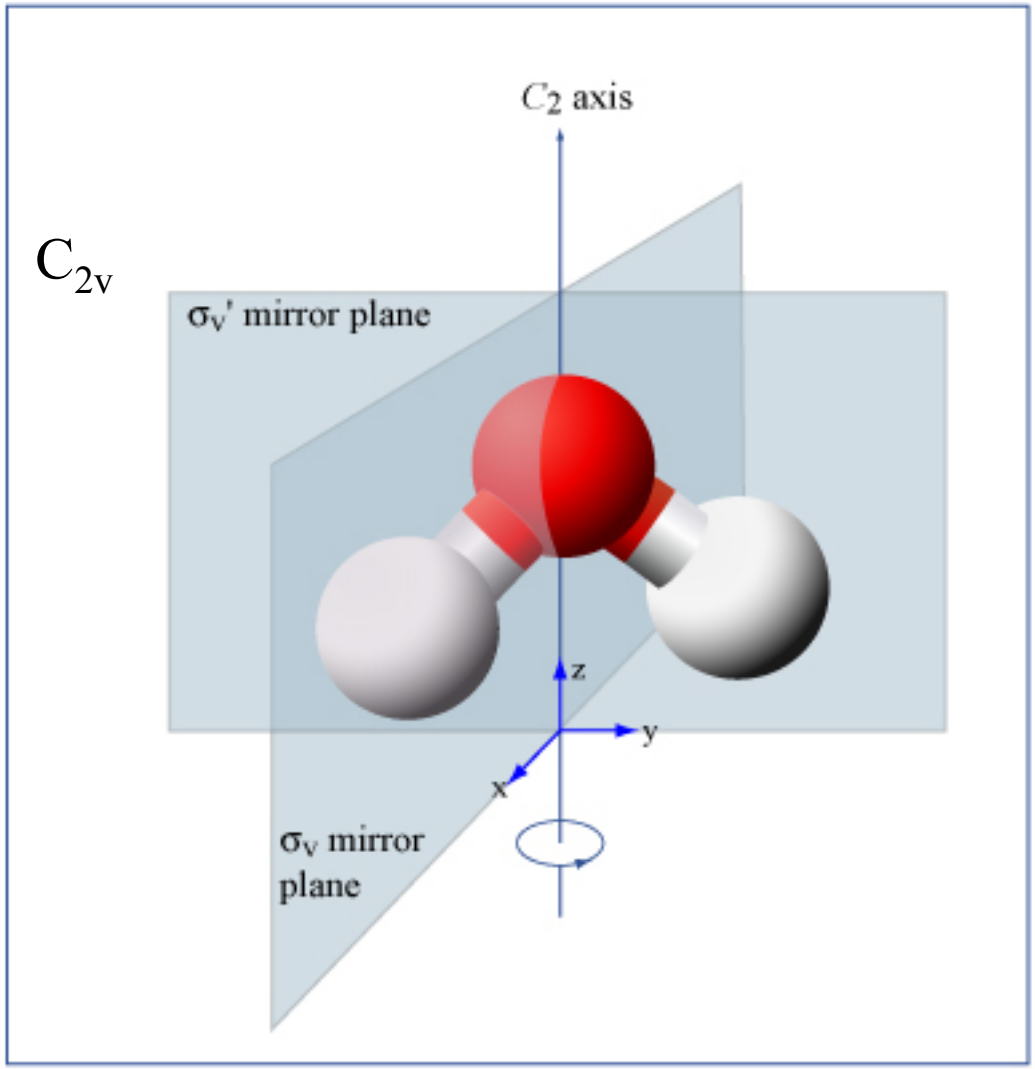
2. Associativity: For all elements in G, (A☼B) ☼C==A☼ (B☼C).

3. Identity: There is an identity element I such that I☼A=A☼I=A for every element A in G.

4. Inverse: There is an inverse or reciprocal of each element. Therefore, the set must contain an element B=inv(A) such that A☼inv(A)=inv(A) ☼A=I for each element of G.

Examples

- Integer numbers, and addition
- Integer numbers, and multiplication
- Real numbers, and multiplication
- Rotations around an axis by 360/n



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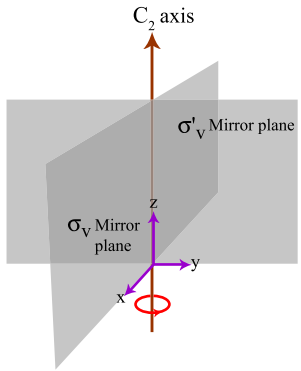
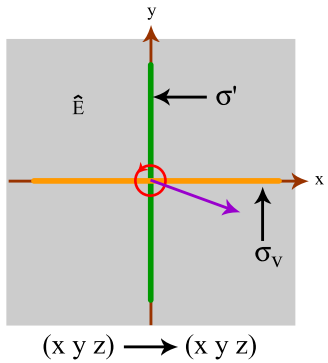
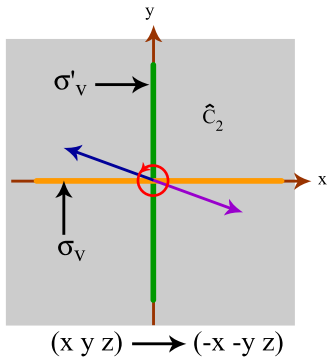
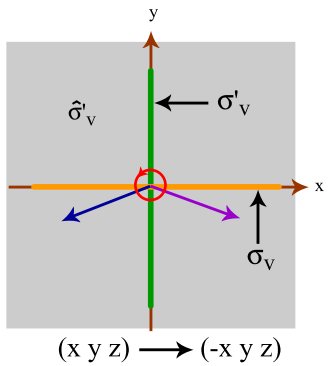
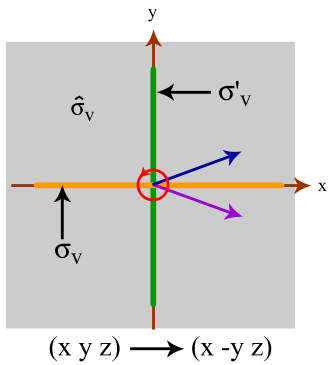
Symmetries of H_2O











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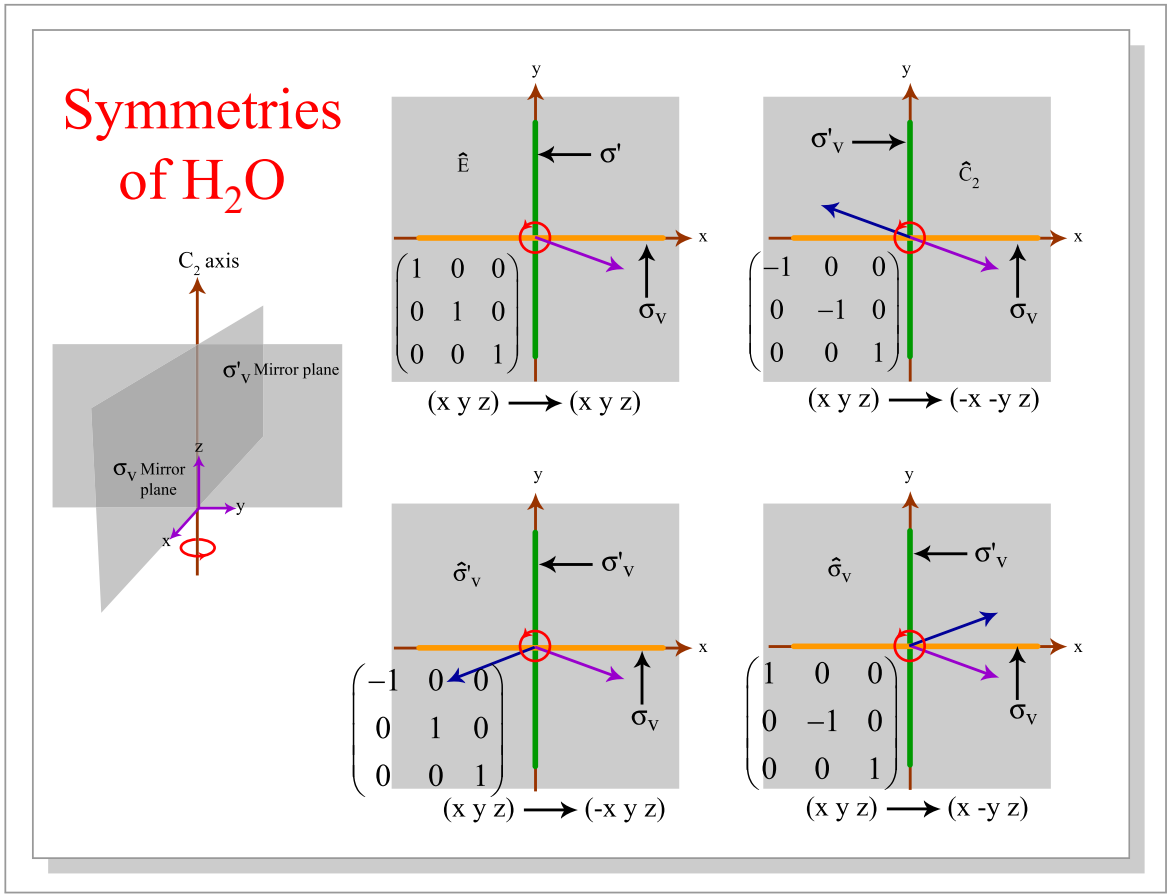

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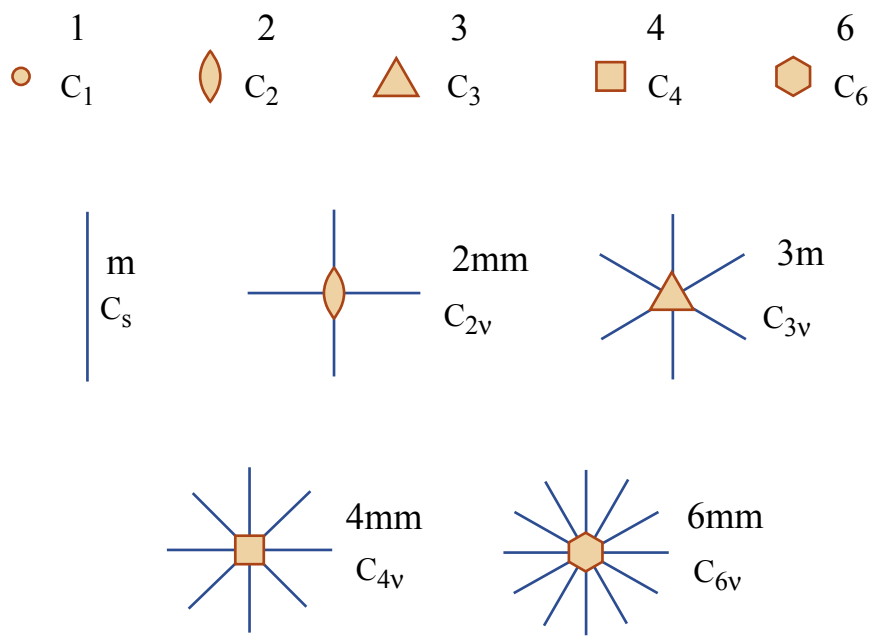
The 4 symmetry operations of H_2O form a group (called C_{2v})

1. Closure: A☼B is also in G.
2. Associativity: (A☼B) ☼C=A☼ (B☼C)
3. Identity: I☼A=A☼I
4. Inverse: A☼inv(A)=inv(A) ☼A=I

Second Operation	First Operation			
	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

Ten *crystallographic* point groups in 2d



The ten crystallographic plan point groups. Upper symbol, international notation; lower symbol, Schoenflies notation (see text).

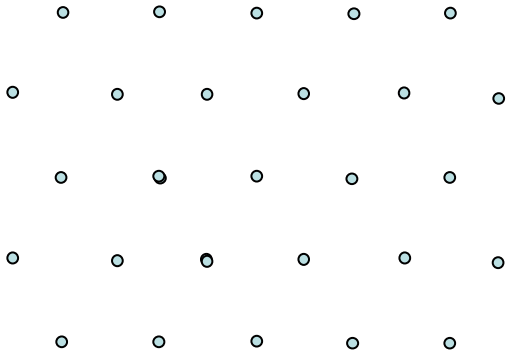
32 *crystallographic* point groups in 3d

The Crystallographic Point Groups and the Lattice Types.

Crystal System	Schoenflies Symbol	Hermann-Mauguin Symbol	Order of the group	Laue Group
Triclinic	C_1	1	1	$\bar{1}$
	C_i	$\bar{1}$	2	
Monoclinic	C_2	2	2	2/*m*
	C_s	*m*	2	
	C_{2h}	2/*m*	4	
Orthorhombic	D_2	222	4	*mmm*
	C_{2v}	*mm*2	4	
	D_{2h}	*mmm*	8	
Tetragonal	C_4	4	4	4/*m*
	S_4	$\bar{4}$	4	
	C_{4h}	4/*m*	8	
	D_4	422	8	4/*m mm*
	C_{4v}	4*mm*	8	
	D_{2d}	$\bar{4}$2*m*	8	
	D_{4h}	4/*m mm*	16	
Trigonal	C_3	3	3	$\bar{3}$
	C_{3i}	$\bar{3}$	6	
	D_3	32	6	$\bar{3}m$
	C_{3v}	3*m*	6	
	D_{3d}	$\bar{3}m$	12	
Hexagonal	C_6	6	6	6/*m*
	C_{3h}	$\bar{6}$	6	
	C_{6h}	6/*m*	12	
	D_6	622	12	6/*m mm*
	C_{6v}	6*mm*	12	
	D_{3h}	$\bar{6}m$2	12	
	D_{6h}	6/*m mm*	24	
Cubic	T	23	12	$m\bar{3}$
	T_h	$m\bar{3}$	24	
	O	432	24	$m\bar{3}m$
	T_d	$4\bar{3}m$	24	
	O_h	$m\bar{3}m$	48	

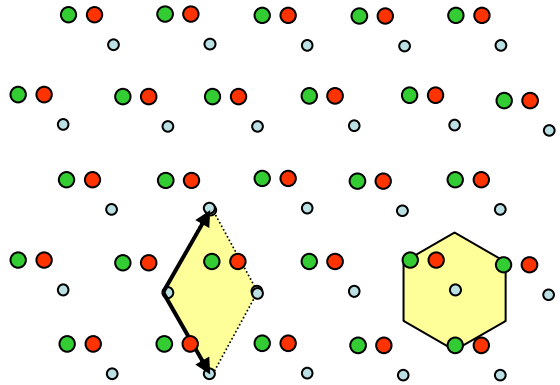
(1) Each component in the name refers to a different direction. For example, the symbol for the orthorhombic group, 222, refers to the symmetry around the *x*, *y*, and *z* axes, respectively.
(2) The position of the symbol *m* indicates the direction perpendicular to the mirror plane.
(3) Fractional symbols mean that the axes of the operators in the numerator and denominator are parallel. For example, 2/*m* means that there is a mirror plane perpendicular to a rotation diad.
(4) For the orthorhombic system, the three symbols refer to the three mutually perpendicular *x*, *y*, and *z* axes, in that order.
(5) All tetragonal groups have a 4 or $\bar{4}$ rotation axis in the *z*-direction and this is listed first. The second component refers to the symmetry around the mutually perpendicular x and *y* axes and the third component refers to the directions in the *x*–*y* plane that bisect the *x* and *y* axes.
(6) In the trigonal systems (which always have a 3 or $\bar{3}$ axis first) and hexagonal systems (which always have a 6 or $\bar{6}$ axis first), the second symbol describes the symmetry around the equivalent directions (either 120° or 60° apart) in the plane perpendicular to the 3, $\bar{3}$, 6, or $\bar{6}$ axis.
(7) A third component in the hexagonal system refers to directions that bisect the angles between the axes specified by the second symbol.
(8) If there is a 3 in the second position, it is a cubic point group. The 3 refers to rotation triads along the four body diagonals of the cube. The first symbol refers to the cube axis and the third to the face diagonals.

Crystal Structure = Lattice + Basis

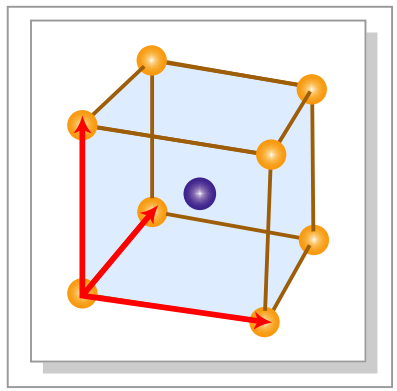


Lattice

Basis



Crystal Structure = Lattice + basis



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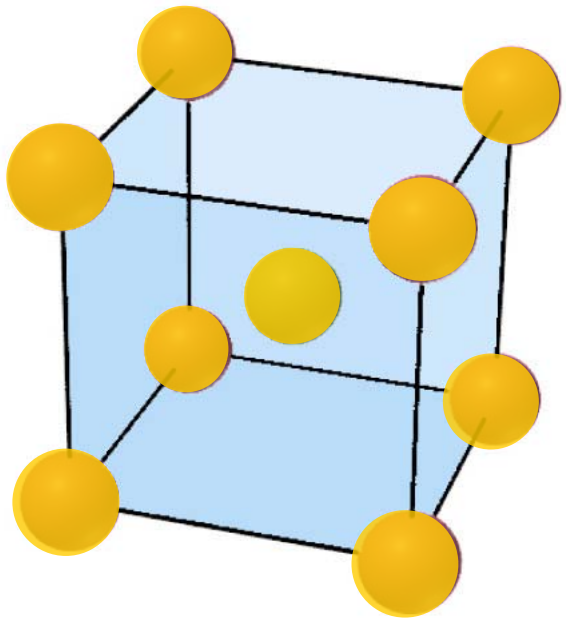
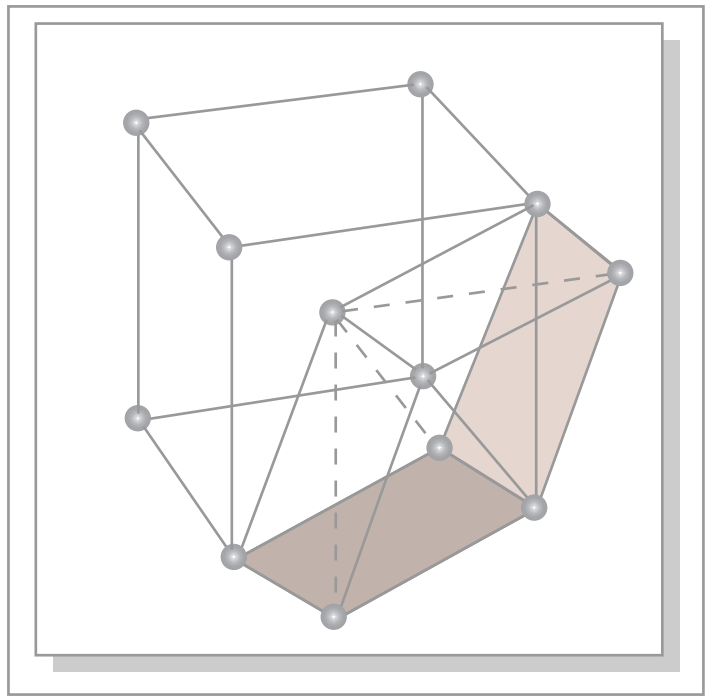
Primitive unit cell and conventional unit cell





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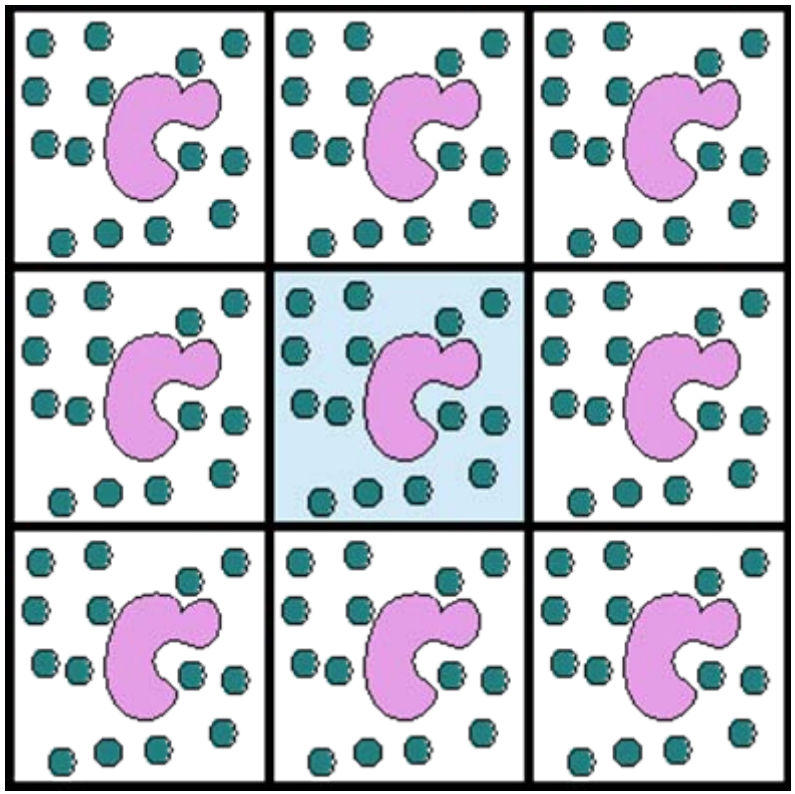
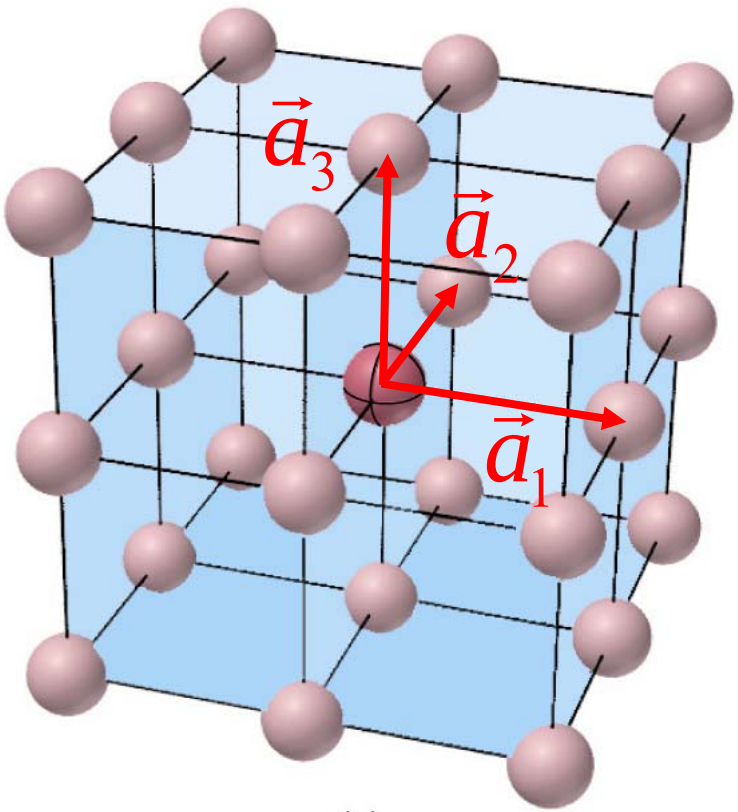
Periodic boundary conditions for the ions (i.e. the ext. potential)



- Unit cell = Bravais lattice = space filler
- Atoms in the unit cell + infinite periodic replicas

Reciprocal lattice (I)

- Let's start with a Bravais lattice, defined in terms of its primitive lattice vectors…



$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

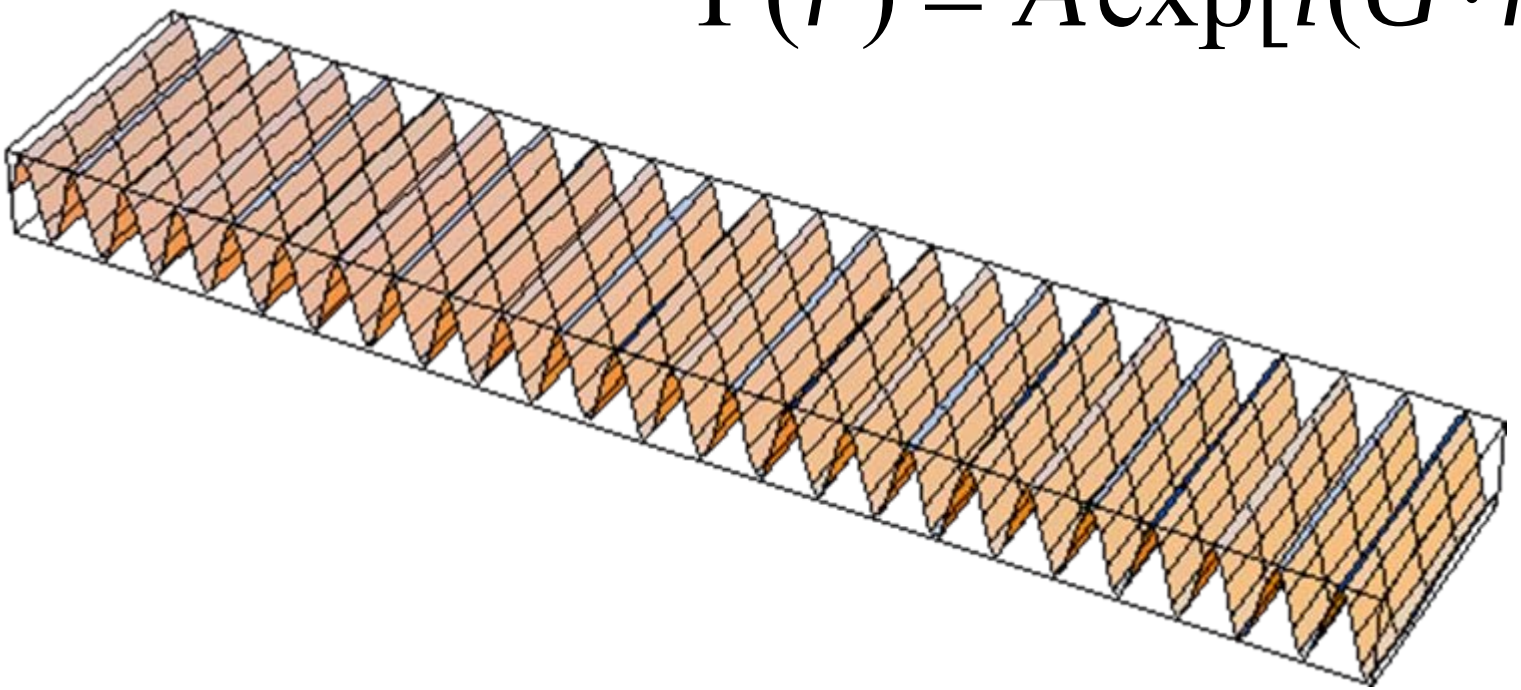
l, m, n integer numbers

$$\vec{R} = (l, m, n)$$

Reciprocal lattice (II)

- …and then let's take a plane wave

$$\Psi(\vec{r}) = A\exp[i(\vec{G}\cdot\vec{r})]$$



Reciprocal lattice (III)

- What are the wavevectors for which our plane wave has the same amplitude at all lattice points ?

$$\exp[i(\vec{G}\cdot\vec{r})] = \exp[i(\vec{G}\cdot(\vec{r}+\vec{R}))]$$

$$\exp[i(\vec{G}\cdot\vec{R})] = 1$$

$$\exp[i(\vec{G}\cdot(l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3))] = 1$$

$\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ define the primitive unit cell

$$\vec{G}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$$

$\vec{G}_1$, $\vec{G}_2$ and $\vec{G}_3$ define the reciprocal space Brillouin Zone

Reciprocal lattice (IV)

$\vec{G}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$ n integer is satisfied by

$\vec{G} = h\vec{b}_1 + i\vec{b}_2 + j\vec{b}_3$ with h, i, j integers,

provided $\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$ $\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$ $\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$

$\vec{G} = (h, i, j)$ are the reciprocal-lattice vectors

Examples of reciprocal lattices

Direct lattice	Reciprocal lattice
Simple cubic	Simple cubic
FCC	BCC
BCC	FCC
Orthorhombic	Orthorhombic

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)}$$