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

$$\boxed{\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right)-\frac{\partial L}{\partial q_j}=0}$$ (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 mv², V=V(x)

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

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



# Hamiltonian

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

CONJUGATE VAR.

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

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

$E(V,S) \rightarrow$

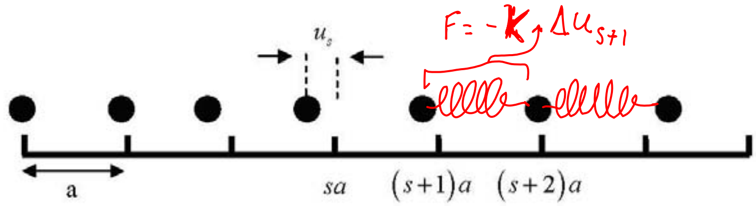
$H = E + PV =$

$= H(P,S)$

$L = T - V$

# 1-dimensional monoatomic chain

$F = -K \Delta u_{s+1}$




$$H = T + V = \sum_s \frac{p_s^2}{2M} + \frac{1}{2} K \sum (u_s - u_{s+1})^2$$

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



$$H = \sum_s H_s \qquad H_s = \frac{p_s^2}{2M} + \frac{1}{2} K (u_s - u_{s+1})^2 + \frac{1}{2} K (u_{s-1} - u_s)^2 + \ldots$$

$$M \frac{d^2 u_s}{dt^2} = K (u_{s+1} - u_{s-1} - 2u_s)$$

$$\boxed{u_s \propto e^{-i\omega t}}$$ ANSATZ

$$-M\omega^2 u_s = K (u_{s+1} + u_{s-1} - 2u_s)$$

$$u_s = u e^{iska}$$

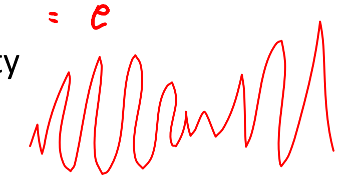
## Properties

- Unique solutions for k in the first BZ

$$\frac{u_s}{u_{s+1}} = \frac{e^{iksa}}{e^{ik(s+1)a}} = e^{-ika} \qquad k \to k + \frac{2\pi}{a}n$$

$$e^{-i\left(k+\frac{2\pi}{a}n\right)a} = e^{-ika}$$

- Phase velocity and group velocity



$$v_{phase} = \frac{\omega}{k} \qquad e^{i(kr-\omega t)} \qquad v_{group} = \frac{d\omega}{dk}$$



## Properties

- Standing waves $\Rightarrow \frac{d\omega}{dk} = 0 \qquad k = \pm\frac{\pi}{a}$

- Long wavelength limit

$$\omega^2(k) = \frac{2K}{M}(1-\underbrace{\cos ka}_{1-\frac{(ka)^2}{2}})$$

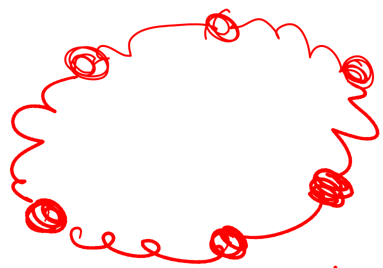
$$ka \ll 1$$

$$\omega^2 = \frac{2K}{M}\frac{(ka)^2}{2} \Rightarrow \omega = \left(\frac{K}{M}\right)^{1/2} ka$$

## Ring geometry

$$\boxed{k = \frac{2\pi}{a}\frac{n}{N}}$$

$kNa = 2n\pi$



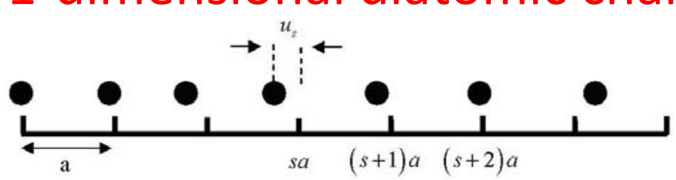
$u_s = u_{s+N}$

$e^{ikNa} = 1$

$$\underbrace{e^{iksa} = e^{ik(s+N)a}}$$



## 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**

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

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

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

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

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.





# Translational Symmetry

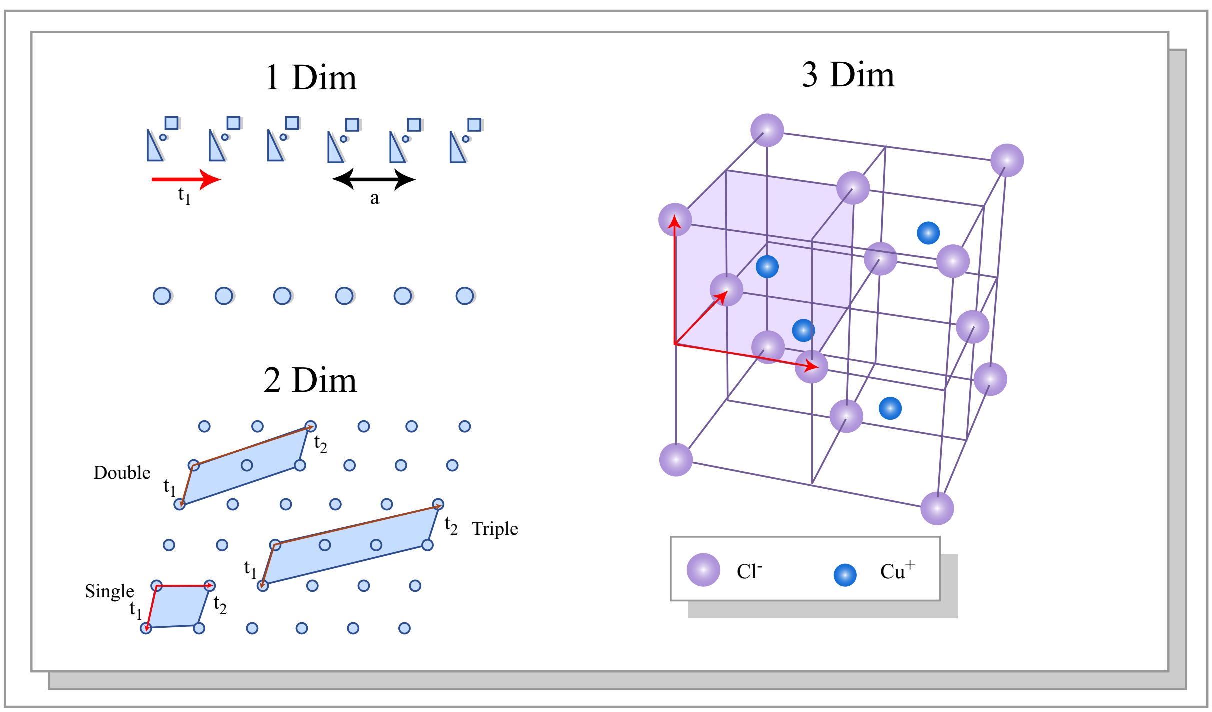



Figure by MIT OpenCourseWare.

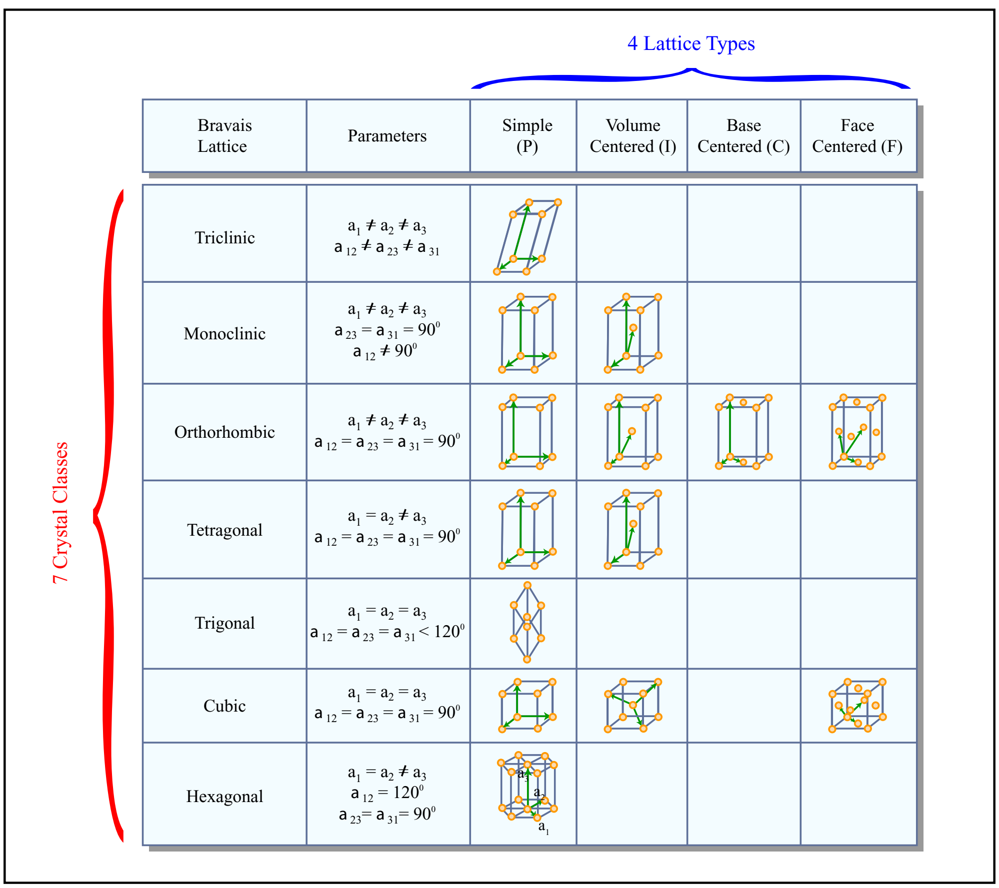
# Bravais Lattices

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

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

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

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




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

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

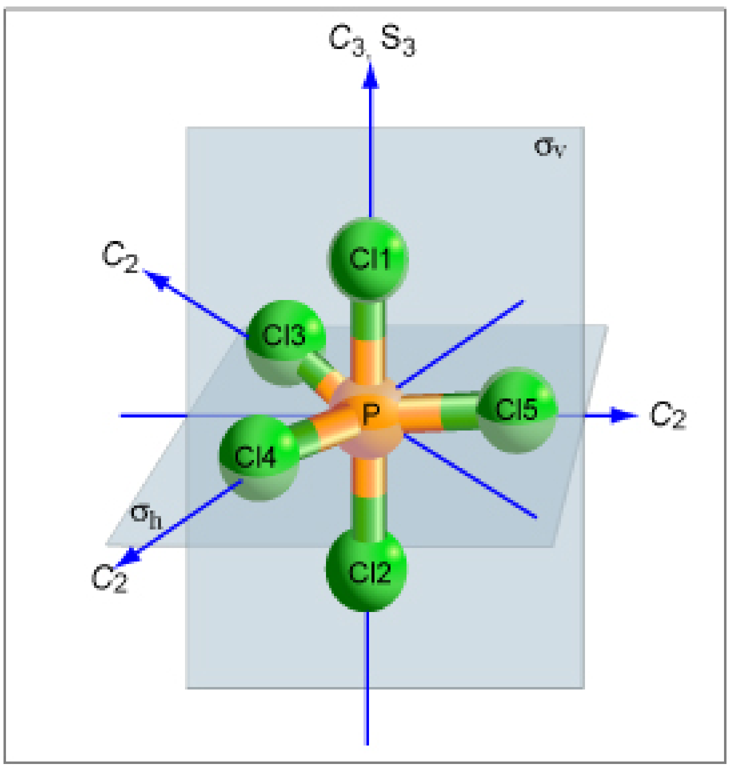



Figure by MIT OpenCourseWare.

# 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 360º /n 1, 2, .... , n times (indicated by superscript) |
| σ | Mirror plane | $\hat{\sigma}$ | reflect through the mirror plane |
| i | Inversion center | $\hat{i}$ | $(x, y, z) \rightarrow (-x, -y, -z)$ |
| $S_n$ | n-Fold rotation-reflection axis | $\hat{S}_n$ | rotate about axis by 360º /n, and reflect through a plane perpendicular to axis. |

Figure by MIT OpenCourseWare.

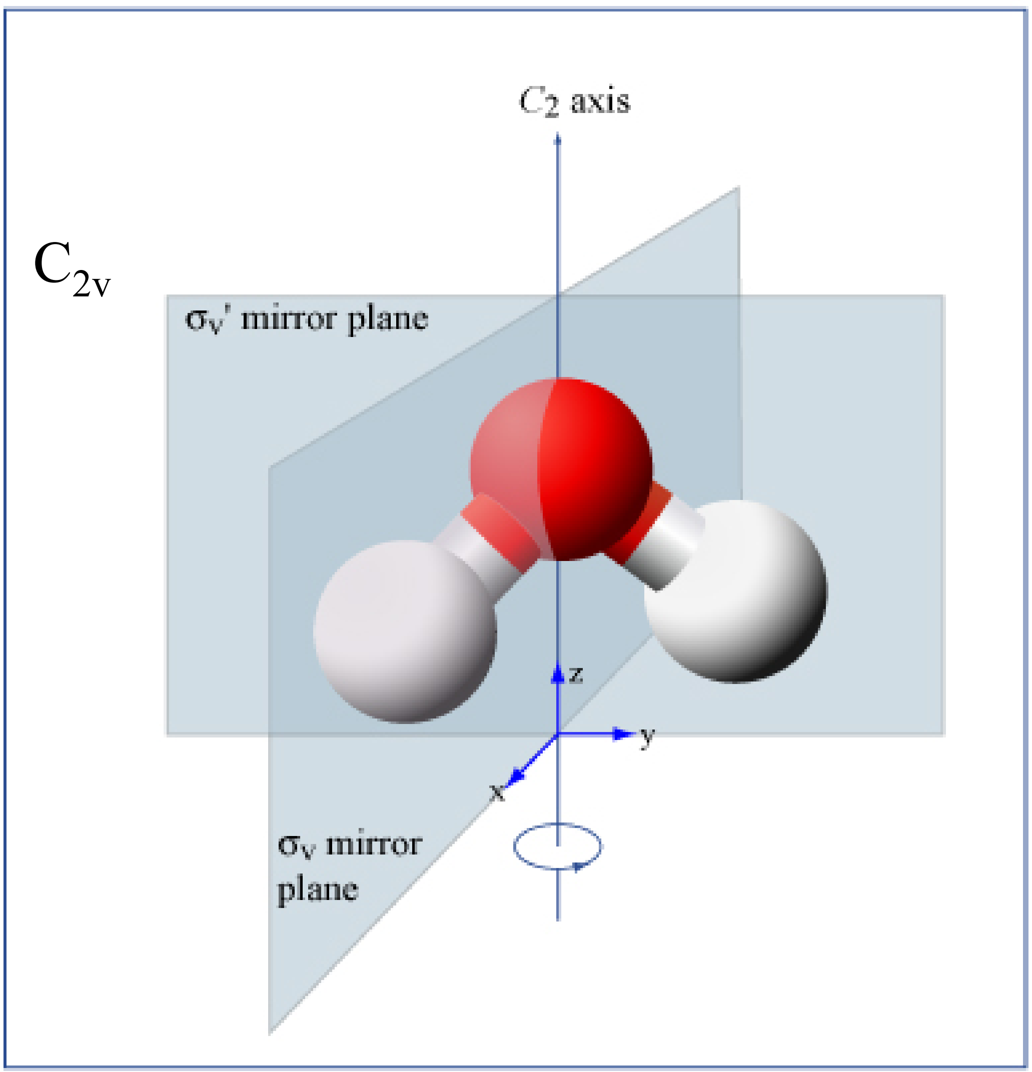
# Group Therapy…

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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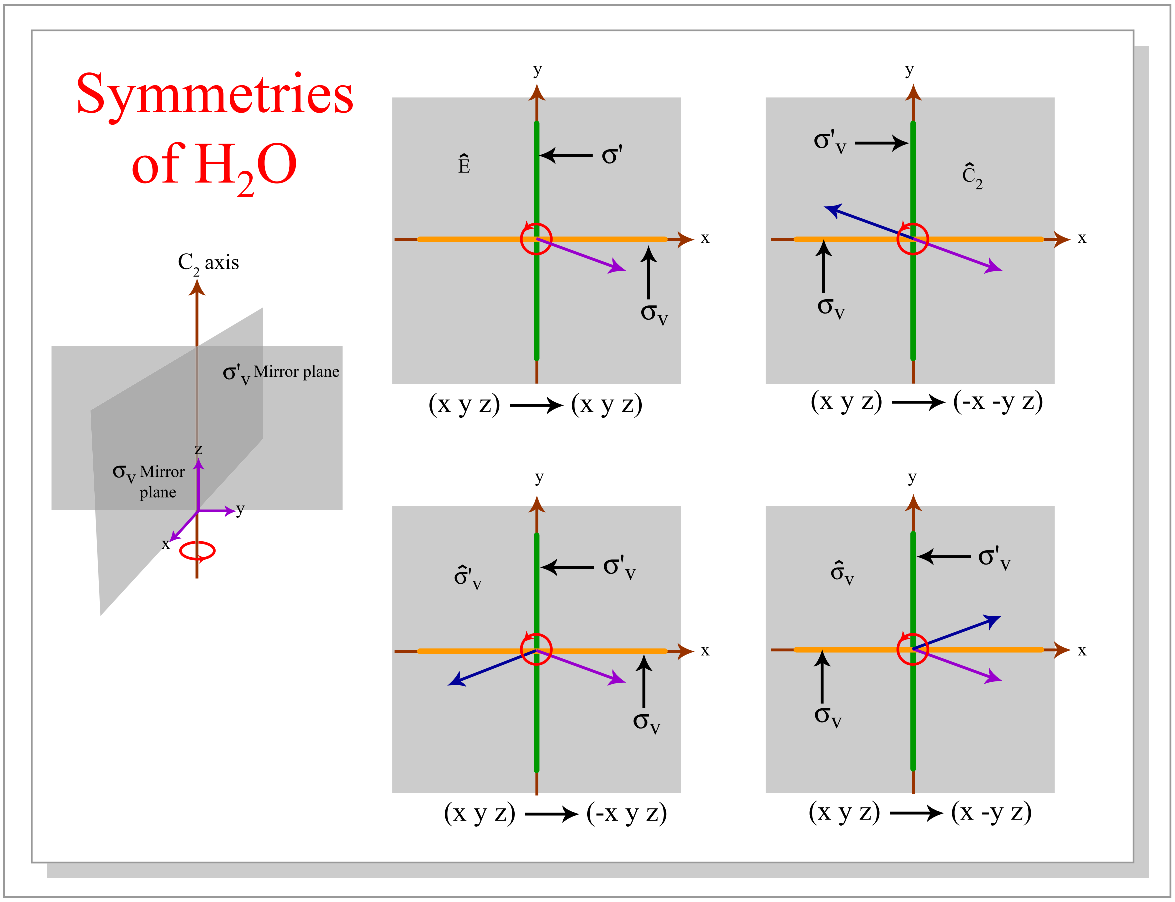


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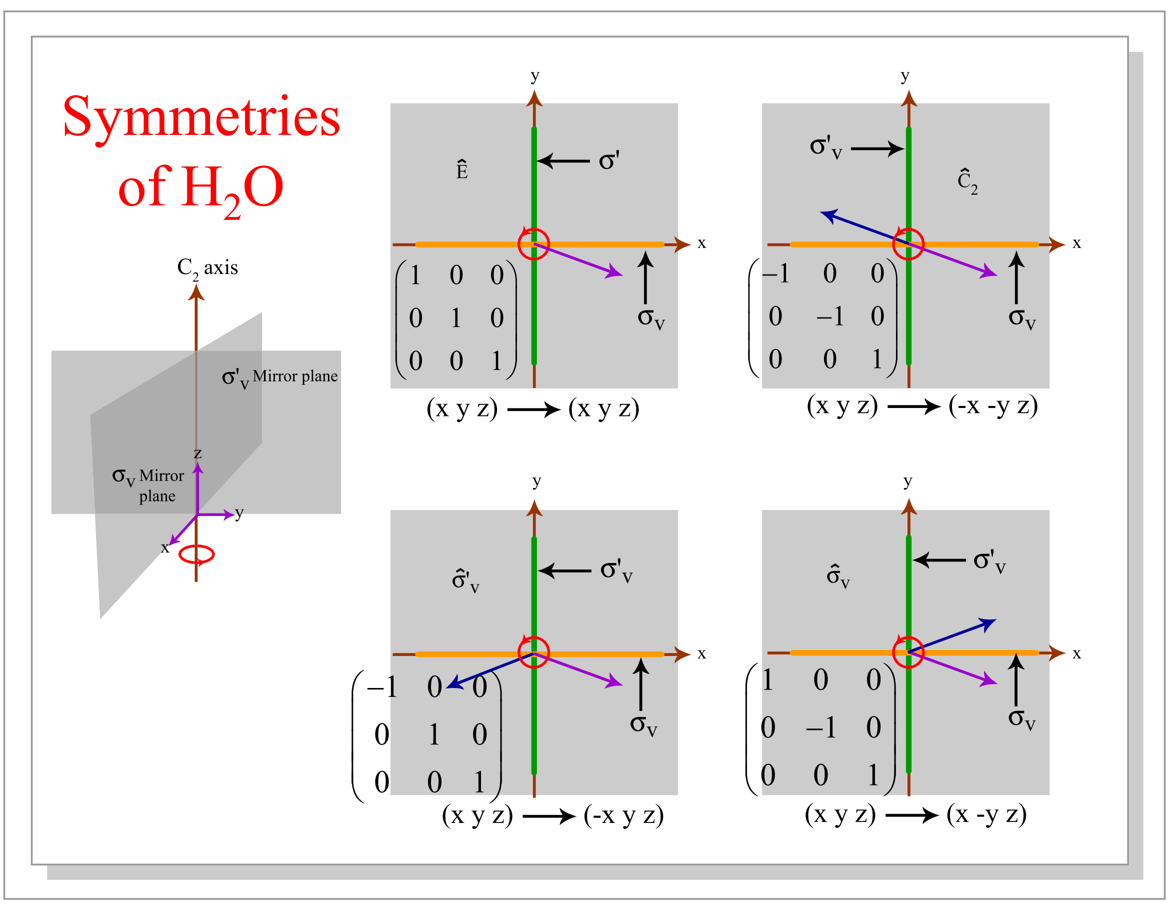



Figure by MIT OpenCourseWare.

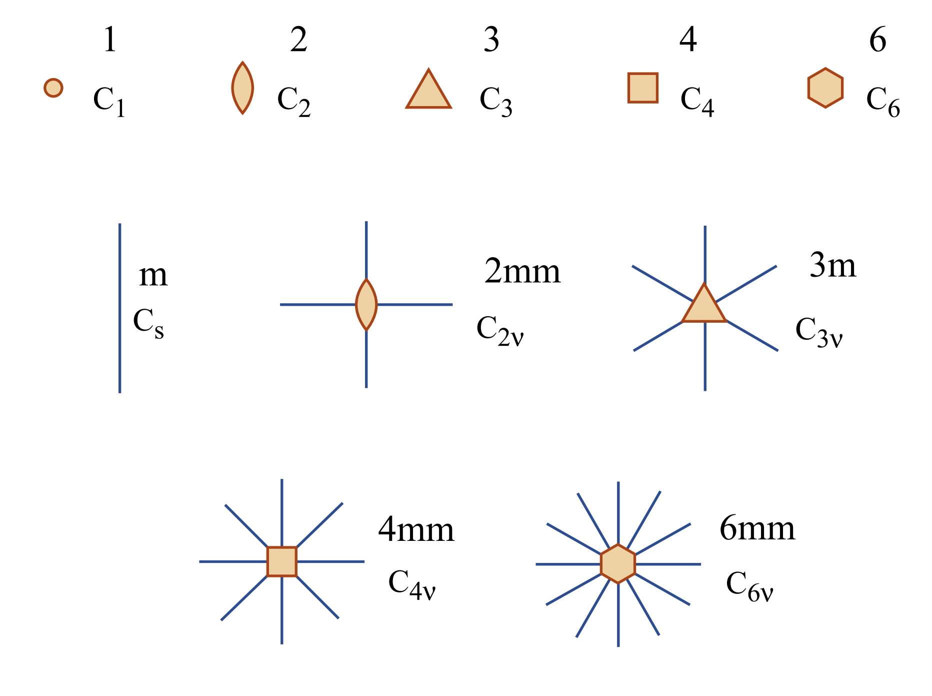
# The 4 symmetry operations of $H_2O$ form a group (called $C_{2v}$)

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 | | | |
|---|---|---|---|---|
| | $\hat{E}$ | $\hat{C}_2$ | $\hat{\sigma}_v$ | $\hat{\sigma}'_v$ |
| $\hat{E}$ | $\hat{E}$ | $\hat{C}_2$ | $\hat{\sigma}_v$ | $\hat{\sigma}'_v$ |
| $\hat{C}_2$ | $\hat{C}_2$ | $\hat{E}$ | $\hat{\sigma}'_v$ | $\hat{\sigma}_v$ |
| $\hat{\sigma}_v$ | $\hat{\sigma}_v$ | $\hat{\sigma}'_v$ | $\hat{E}$ | $\hat{C}_2$ |
| $\hat{\sigma}'_v$ | $\hat{\sigma}'_v$ | $\hat{\sigma}_v$ | $\hat{C}_2$ | $\hat{E}$ |

Figure by MIT OpenCourseWare.

# Ten *crystallographic* point groups in 2d




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

Figure by MIT OpenCourseWare.

The Crystallographic Point Groups and the Lattice Types.

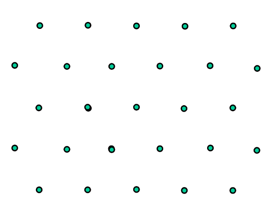
| Crystal System | Schoenflies Symbol | Hermann-Mauguin Symbol | Order of the group | Laue Group |
|---|---|---|---|---|
| **Triclinic** | $C_1$ | $1$ | 1 | $\bar{1}$ |
| | $C_i$ | $\bar{1}$ | 2 | |
| **Monoclinic** | $C_2$ | $2$ | 2 | $2/m$ |
| | $C_s$ | $m$ | 2 | |
| | $C_{2h}$ | $2/m$ | 4 | |
| **Orthorhombic** | $D_2$ | $222$ | 4 | $mmm$ |
| | $C_{2v}$ | $mm2$ | 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 | $4/m\ mm$ |
| | $C_{4v}$ | $4mm$ | 8 | |
| | $D_{2d}$ | $\bar{4}2m$ | 8 | |
| | $D_{4h}$ | $4/m\ mm$ | 16 | |
| **Trigonal** | $C_3$ | $3$ | 3 | $\bar{3}$ |
| | $C_{3i}$ | $\bar{3}$ | 6 | |
| | $D_3$ | $32$ | 6 | $\bar{3}m$ |
| | $C_{3v}$ | $3m$ | 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 | $6/m\ mm$ |
| | $C_{6v}$ | $6mm$ | 12 | |
| | $D_{3h}$ | $\bar{6}m2$ | 12 | |
| | $D_{6h}$ | $6/m\ mm$ | 24 | |
| **Cubic** | $T$ | $23$ | 12 | $m\bar{3}$ |
| | $T_h$ | $m\bar{3}$ | 24 | |
| | $O$ | $432$ | 24 | $m\bar{3}m$ |
| | $T_d$ | $\bar{4}3m$ | 24 | |
| | $O_h$ | $m\bar{3}m$ | 48 | |

## 32 *crystallographic* point groups in 3d

(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.

Figure by MIT OpenCourseWare.

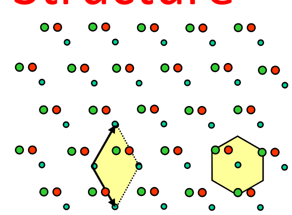
## Crystal Structure = Lattice + Basis



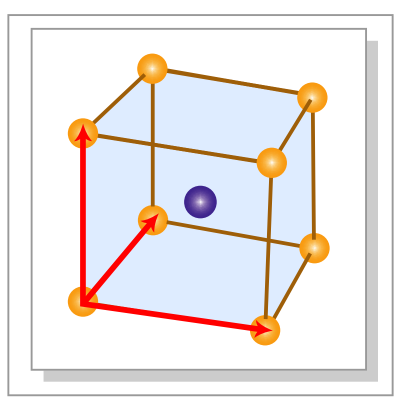
Lattice



Basis



Crystal Structure = Lattice + basis



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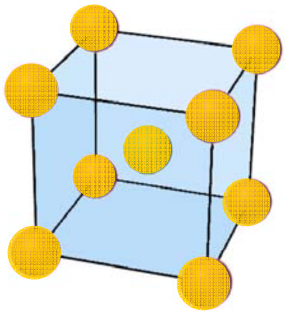
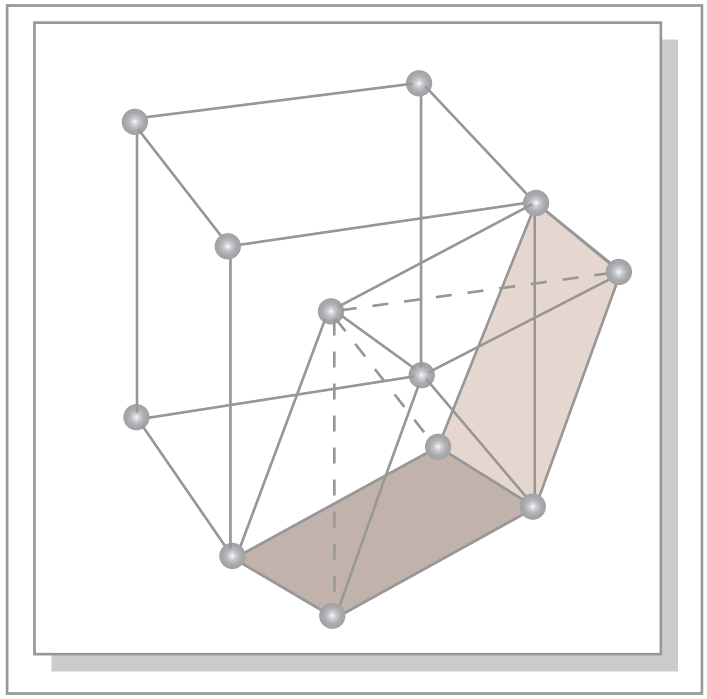
## Primitive unit cell and conventional unit cell





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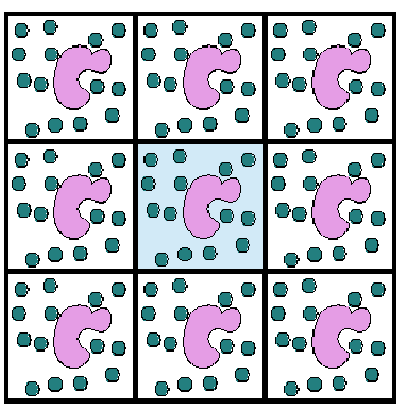
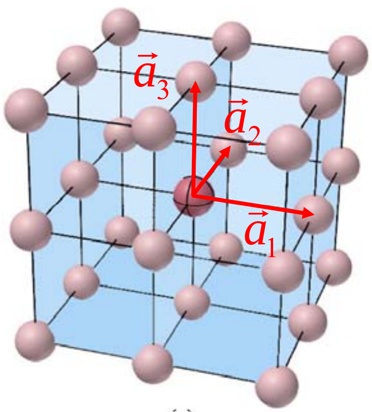
## Periodic boundary conditions for the ions (i.e. the ext. potential)



- 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…

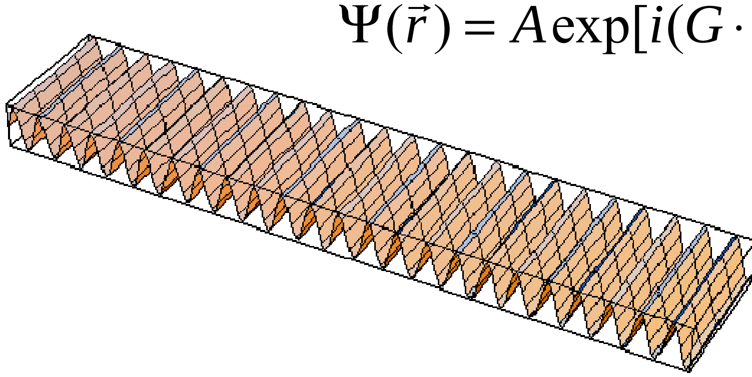



$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$
$$l, m, n \text{ integer numbers}$$
$$\vec{R} = (l, m, n)$$

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

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

# Examples of reciprocal lattices

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

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