

# Brief Reminder

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

$$\Psi = \Psi(\{\mathbf{R}_i\}, \{r_i, \sigma_i\})$$

↑  
Born-Oppenheimer approx.

The electronic Hamiltonian:

1) Kinetic energy

$$T = \sum_{K=1}^N \frac{\hbar^2}{2m} \nabla_K^2$$

2) Coulomb interaction

i) Nucleus-nucleus

$$\frac{1}{2} \sum_{I, J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

(i) Ion-electron

$$\sum_{I=1}^M \sum_{K=1}^N v^{\text{ion}}(|\mathbf{R}_I - \mathbf{r}_K|)$$

iii) Electron-electron

$$\frac{1}{2} \sum_{\mathbf{k}, \mathbf{k}'}^N \frac{1}{|\vec{r}_{\mathbf{k}} - \vec{r}_{\mathbf{k}'}|}$$

← HARD PART

NEEDS APPROXIMATION

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Approximations to the Schrödinger equation:

1) Hartree approximation

$$V_{\text{Hartree}}(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r'$$

mean-field treatment

2) Hartree-Fock approximation

$$\Psi^{\text{HF}}(\{\vec{r}_i \sigma_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{1\sigma_1}(\vec{r}_1 \sigma_1) & \dots & \psi_{1\sigma_N}(\vec{r}_1 \sigma_N) \\ \psi_{2\sigma_1}(\vec{r}_2 \sigma_1) & \dots & \psi_{2\sigma_N}(\vec{r}_2 \sigma_N) \\ \vdots & & \vdots \\ \psi_{N\sigma_1}(\vec{r}_N \sigma_1) & \dots & \psi_{N\sigma_N}(\vec{r}_N \sigma_N) \end{vmatrix}$$

### 3) Density-functional theory

In principle, exact

$$\hat{H} = T_S + V^{\text{eff}} + V^{\text{Hartree}} + V^{\text{xc}}$$

$$\Downarrow$$
$$\left\{ -\frac{\hbar}{2m} \nabla^2 + V^{\text{eff}}(\vec{r}) \right\} \psi_{0i}(\vec{r}) = \epsilon_{0i} \psi_{0i}(\vec{r})$$

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## Chapter 4 Lattice periodicity

### 4.1. Symmetry

$$h \psi_{0i}(\vec{r}) = \epsilon_{0i} \psi_{0i}(\vec{r})$$

$$h = -\frac{\hbar}{2m} \nabla^2 + V^{\text{eff}}(\vec{r})$$

$$V^{\text{eff}}(\vec{r}) = \underbrace{V^{\text{Hartree}}(\vec{r}) + V^{\text{xc}}(\vec{r})}_{\text{symmetry is given by } h(\vec{r})}$$

$\nabla^2$  is invariant to translations, rotations, and inversions in real space

$\Rightarrow$  the symmetry is determined by  $V^{\text{eff}}(\vec{r})$

$$\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$n_i \in \mathbb{Z}$ ,  $\vec{a}_i$  are linearly independent

Define  $T_{\vec{R}_n} f(\vec{r}) = f(\vec{r} + \vec{R}_n)$

$$T_{\vec{R}_n} \psi^{\text{eH}}(\vec{r}) = \psi^{\text{eH}}(\vec{r} + \vec{R}_n) = \psi^{\text{eH}}(\vec{r})$$

and  $T_{\vec{R}_n} \nabla^2 f(\vec{r}) = \nabla^2 f(\vec{r} + \vec{R}_n) = \nabla^2 T_{\vec{R}_n} f(\vec{r})$

$\Leftrightarrow T_{\vec{R}_n}$  and  $h$  commute

Then,

$$T_{\vec{R}_n} h \rho_i(\vec{r}) = h \rho_i(\vec{r} + \vec{R}_n)$$

$$= h T_{\vec{R}_n} \rho_i(\vec{r}) = \sum \rho_i(\vec{r} + \vec{R}_n)$$

### Definitions

Vectors  $\vec{a}_i$  are called the primitive vectors

The set of all points  $\{\vec{R}_n\}$  is called

Bravais lattice

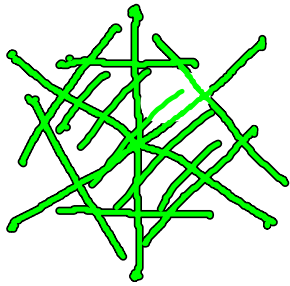
The choice of  $\vec{a}_i$  is not unique

Not all sets of symmetric points generate a Bravais lattice.

## Wigner-Seitz Cell

Contains <sup>exactly</sup> one point of the  
Bravais lattice

Wigner-Seitz cell: A region that is  
closer to any given lattice point than to  
all other points  $\{R_n\}$



## Symmetry operations

Apart from translations (rigid shift)  
there are other symmetry operations:

1)  $R_p$  - rotation

1a)  $C_n$  - normal rotation by  $\phi = \frac{2\pi}{n}$

1b)  $S_n$  - improper rotation

- 2)  $\sigma$  - reflection
- 3)  $i = \sigma_2$  inversion through a point
- 4)  $\hat{T}R_\theta$  - screw rotations
- 5)  $\hat{T}\sigma$  - glide reflection

The set of symmetry operations forms a group.

### Point group of a cube

$O_h$  with  $O$  meaning octahedra

symbol	operation	number
$E$	unity	1
$C_4$	rot around an axis by $\frac{\pi}{2}$	6
$C_2$	..... axis by $\pi$	3
$C_2$	rot around six axis. cut the edges in the middle by $\pi$	6
$C_3$	rot. around space diagonal by $\pm \frac{2\pi}{3}$	8
$\otimes i$	inversion	24
		48 $O_h$

There is a finite number of symmetry operations for any Bravais lattice.

{ Only 4 allowed rotations :

$C_2, C_3, C_4, C_6$

✓ Crystallographic restriction theorem

Proof: Two point  $A, B$  in the Bravais lattice

$$\vec{A} - \vec{B} = \vec{r}$$

After rotation by  $\alpha$  :  $\vec{A} \rightarrow \vec{A}'$   
 $\vec{B} \rightarrow \vec{B}'$

$\vec{A}', \vec{B}' \in$  Bravais lattice

$$\vec{A}' - \vec{B}' = \vec{r}'$$

$$\vec{r}' = n\vec{r} \quad (1)$$

$$\Rightarrow |\vec{r}'| = -2|\vec{r}|\cos(\alpha) + |\vec{r}| \quad (2)$$

Combining (1) and (2)

$$\cos(\alpha) = (1-n)/2 = \frac{N}{2}, \quad N \in \mathbb{Z}$$

$$|\cos(\alpha)| \leq 1 \Rightarrow |N| \leq 2$$

$$\Rightarrow 0 \leq \alpha \leq 180^\circ \Rightarrow \alpha = 0^\circ, 60^\circ, 90^\circ, 120^\circ, 160^\circ$$

This restriction was limited for

quasi-crystals in 1984

PRL 53, 1951 (1984)