Brief Reminder

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

$$\Psi = \Psi\left(\{R_i\}, \{r_i, \sigma_i\}\right)$$

↑ Born-Oppenheimer approx.

The electronic Hamiltonian:

1) Kinetic energy

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

2) Coulomb interaction

i) Nucleus-nucleus

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

ii) Ion-electron

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

iii) Electron-electron

$$\frac{1}{2}\sum_{k,k'}{}' \frac{1}{|\vec{r}_k - \vec{r}_{k'}|}$$ ← HARD PART

NEEDS APPROXIMAT

Approximations to the Schrödinger equation:

1) Hartree approximation

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

mean-field treatment

2) Hartree-Fock approximation

$$\psi^{HF}(\{\vec{r}_i \sigma_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\sigma_1 s_1}(\vec{r}_1 \sigma_1) & \cdots & \phi_{\sigma_N s_N}(\vec{r}_1 \sigma_1) \\ \phi_{\sigma_2 s_1}(\vec{r}_2 \sigma_2) & \cdots & \phi_{\sigma_N s_N}(\vec{r}_2 \sigma_2) \\ \vdots & & \\ \phi_{\sigma_1 s_1}(\vec{r}_N \sigma_N) & \cdots & \phi_{\sigma_N s_N}(\vec{r}_N \sigma_N) \end{vmatrix}$$

3) Density-functional theory

In principle, exact

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

$$\Big\{ -\frac{\hbar}{2m}\nabla^2 + V^{eff}(\vec{r}) \Big\} \psi_{o_i}(\vec{r}) = \varepsilon_{o_i} \psi_{o_i}(\vec{r})$$

Chapter 4 Lattice periodicity

4.1. Symmetry

$$h\,\psi_{o_i}(\vec{r}) = \varepsilon_{o_i}\,\psi_o(\vec{r})$$

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

$$V^{eff}(\vec{r}) = V^{Hartree}(\vec{r}) + V^{xc}(\vec{r})$$

symmetry is given by $n(\vec{r})$

∇^2 is invariant to translations, rotations, and inversions in real space

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

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

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

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

$$T_{\vec{R}_n} v^{eff}(\vec{r}) = v^{eff}(\vec{r} + \vec{R}_n) = v^{eff}(\vec{r})$$

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, $T_{\vec{R}_n} h \psi_{o_i}(\vec{r}) = h \psi_{o_i}(\vec{r} + \vec{R}_n)$

$= h T_{\vec{R}_n} \psi_{o_i}(\vec{r}) = \varepsilon_{o_i} \psi_{o_i}(\vec{r} + \vec{R}_n)$

Definitions

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

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

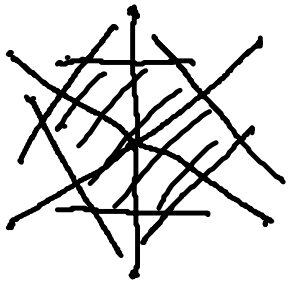
The choice of $\vec{a}_i$ is not unique

Not all sets of symmetric points generate a Bravais lattice.

Wigner - Seitz Cell

Contains exactly 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_ϕ - rotation

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

1b) S_n - improper rotation

2) σ – reflection

3) $i = S_2$ inversion through a point

4) $\hat{T}R_\varphi$ – screw rotation

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	..... by π	3
C_2	rot around six axis. cut the edges in the middle by π	6
C_3	rot. around space diagon. by $\pm\frac{2\pi}{3}$	8
⊗ 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 α: $\vec{A} \to \vec{A}'$, $B \to \vec{B}'$

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

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

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

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

Combining (1) and (2)

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

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

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

This restriction was eliminated for quasi-crystals in 1984

PRL 53, 1951 (1984).