## PHY 752 Solid State Physics
## 11-11:50 AM MWF Olin 107

### Plan for Lecture 19:

**Review of Chapters 1-10**

1. Brief review
2. Discussion of some HW problems
3. Distribute exam



| | | | | | |
|---|---|---|---|---|---|
| 9 | Wed: 02/04/2015 | Chap. 8 | Electronic structure; LCAO and tight binding | #9 | 02/06/2015 |
| 10 | Fri: 02/06/2015 | Chap. 8 | Band structure examples | #10 | 02/09/2015 |
| 11 | Mon: 02/09/2015 | Chap. 9 | Electron-electron interactions | #11 | 02/11/2015 |
| 12 | Wed: 02/11/2015 | Chap. 9 | Electron-electron interactions | #12 | 02/13/2015 |
| 13 | Fri: 02/13/2015 | Chap. 9 | Electron-electron interactions | #13 | 02/16/2015 |
| 14 | Mon: 02/16/2015 | Chap. 10 | Electronic structure calculation methods | #14 | 02/18/2015 |
| 15 | Wed: 02/18/2015 | Chap. 10 | Electronic structure calculation methods | #15 | 02/20/2015 |
| 16 | Fri: 02/20/2015 | Chap. 10 | Electronic structure calculation methods | #16 | 02/23/2015 |
| 17 | Mon: 02/23/2015 | Chap. 10 | Electronic structure calculation methods | #17 | 02/25/2015 |
| 18 | Wed: 02/25/2015 | Chap. 10 | Electronic structure calculation methods | #18 | 02/27/2015 |
| 19 | Fri: 02/27/2015 | Chap. 1-3,7-10 | Review; Take-home exam distributed | | |
| | Mon: 03/02/2015 | *APS Meeting* | Take-home exam (no class meeting) | | |
| | Wed: 03/04/2015 | *APS Meeting* | Take-home exam (no class meeting) | | |
| | Fri: 03/06/2015 | *APS Meeting* | Take-home exam (no class meeting) | | |
| | Mon: 03/09/2015 | *Spring break* | | | |
| | Wed: 03/11/2015 | *Spring break* | | | |
| | Fri: 03/13/2015 | *Spring break* | | | |
| 20 | Mon: 03/16/2015 | | | | |



Review

**Introduction to crystalline solids**

- An ideal crystal fills all space
  - Limited possibilities for crystalline forms –
    - ❑ Only 14 Bravais lattices
    - ❑ Only 32 crystallographic point groups
    - ❑ Only 230 distinct crystallographic structures

Bravais lattice translation vectors

$$\mathbf{T}=n_1\mathbf{T}_1+n_2\mathbf{T}_2+n_3\mathbf{T}_3$$

Reciprocal lattice vectors

$$\mathbf{G}=n_1\mathbf{G}_1+n_2\mathbf{G}_2+n_3\mathbf{G}_3$$

$$\mathbf{G}_1=2\pi\frac{\mathbf{T}_2\times\mathbf{T}_3}{\mathbf{T}_1\cdot(\mathbf{T}_2\times\mathbf{T}_3)}$$

Note that: $\mathbf{T}_i\cdot\mathbf{G}_j=2\pi\delta_{ij}$

Specification of an atom within the lattice

$$\mathbf{r}_i = \underbrace{\boldsymbol{\tau}_{\text{type}}}_{\text{basis vector}} + \underbrace{n_{1i}\mathbf{a}_1 + n_{2i}\mathbf{a}_2 + n_{3i}\mathbf{a}_3}_{\text{Bravais lattice}}$$



**Short digression on abstract group theory**

What is group theory ?

**A group is a collection of "elements" – $A, B, C, \ldots$ and a "multiplication" process. The abstract multiplication $(\cdot)$ pairs two group elements, and associates the "result" with a third element. (For example $(A \cdot B = C)$.) The elements and the multiplication process must have the following properties.**

1. The collection of elements is closed under multiplication. That is, if elements $A$ and $B$ are in the group and $A \cdot B = C$, element $C$ must be in the group.
2. One of the members of the group is a "unit element" $(E)$. That is, for any element $A$ of the group, $A \cdot E = E \cdot A = A$.
3. For each element $A$ of the group, there is another element $A^{-1}$ which is its "inverse". That is $A \cdot A^{-1} = A^{-1} \cdot A = E$.
4. The multiplication process is "associative". That is for sequential mulplication of group elements $A$, $B$, and $C$, $(A \cdot B) \cdot C = A \cdot (B \cdot C)$.

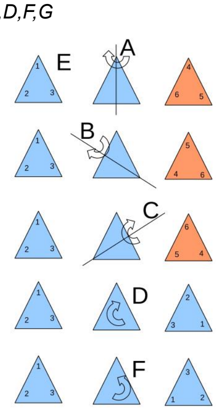


Example of a 6-member group *E,A,B,C,D,F,G*

**Group multiplication table**

**Group of order 6**

| | E | A | B | C | D | F |
|---|---|---|---|---|---|---|
| E | E | A | B | C | D | F |
| A | A | E | D | F | B | C |
| B | B | F | E | D | C | A |
| C | C | D | F | E | A | B |
| D | D | C | A | B | F | E |
| F | F | B | C | A | E | D |



| | E | A | B | C | D | F |
|---|---|---|---|---|---|---|
| E | E | A | B | C | D | F |
| A | A | E | D | F | B | C |
| B | B | F | E | D | C | A |
| C | C | D | F | E | A | B |
| D | D | C | A | B | F | E |
| F | F | B | C | A | E | D |

Check on group properties:
1. Closed; multiplication table uniquely generates group members.
2. Unit element included.
3. Each element has inverse.
4. Multiplication process is associative.

**Definitions**

**Subgroup**: members of larger group which have the property of a group

**Class:** members of a group which are generated by the construction

$$\mathcal{C} = X_i^{-1} Y X_i \quad \text{where } X_i \text{ and } Y \text{ are group elements}$$



Group theory – some comments
- The elements of the group may be abstract; in general, we will use them to describe symmetry properties of our system

Representations of a group

A representation of a group is a set of matrices (one for each group element) -- $\Gamma(A), \Gamma(B)$... that satisfies the multiplication table of the group. The dimension of the matrices is called the dimension of the representation.



Example:

| | E | A | B | C | D | F |
|---|---|---|---|---|---|---|
| E | E | A | B | C | D | F |
| A | A | E | D | F | B | C |
| B | B | F | E | D | C | A |
| C | C | D | F | E | A | B |
| D | D | C | A | B | F | E |
| F | F | B | C | A | E | D |

Note that the one-dimensional "identical representation"

$\Gamma^1(A) = \Gamma^1(B) = \Gamma^1(C) = \Gamma^1(D) = \Gamma^1(E) = \Gamma^1(F) = 1$ is always possible

Another one-dimensional representation is

$$\Gamma^2(A) = \Gamma^2(B) = \Gamma^2(C) = -1$$

$$\Gamma^2(E) = \Gamma^2(D) = \Gamma^2(F) = 1$$

Example:

| | E | A | B | C | D | F |
|---|---|---|---|---|---|---|
| E | E | A | B | C | D | F |
| A | A | E | D | F | B | C |
| B | B | F | E | D | C | A |
| C | C | D | F | E | A | B |
| D | D | C | A | B | F | E |
| F | F | B | C | A | E | D |

A two-dimensional representation is

$$\Gamma^3(E)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \quad \Gamma^3(A)=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$\Gamma^3(B)=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix} \quad \Gamma^3(C)=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix}$$

$$\Gamma^3(D)=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix} \quad \Gamma^3(F)=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}$$



The great orthogonality theorem

Notation: $h \equiv$ order of the group

$R \equiv$ element of the group

$\Gamma^i(R)_{\alpha\beta} \equiv$ $i$th representation of $R$

${}_{\alpha\beta}$ denote matrix indices

$l_i \equiv$ dimension of the representation

$$\sum_R \left(\Gamma^i(R)_{\mu\nu}\right)^* \Gamma^j(R)_{\alpha\beta} = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}\delta_{\nu\beta}$$



Analysis shows that

$$\sum_i l_i^2 = h$$

Simplified analysis in terms of the “characters” of the representations

$$\chi^j(R) \equiv \sum_{\mu=1}^{l_j} \Gamma^j(R)_{\mu\mu}$$

Character orthogonality theorem

$$\sum_R \left(\chi^i(R)\right)^* \chi^j(R) = h\delta_{ij}$$

Note that all members of a class have the same character for any given representation *i.*

Summary of relationships between the characters and classes of a group which follow from the great orthogonality theorem

$$\sum_{e} N_e \left(\chi^i(\mathcal{C})\right)^* \chi^j(\mathcal{C}) = h\delta_{ij}$$

$$\sum_{i} \left(\chi^i(\mathcal{C}_a)\right)^* \chi^i(\mathcal{C}_b) = \frac{h}{N_{\mathcal{C}_a}}\delta_{ab}$$

These results also imply that the number of classes is the same as the number of characters in a group.



Character table for this group:

| | E | A,B,C | D,F |
|---|---|---|---|
| $\chi^1$ | 1 | 1 | 1 |
| $\chi^2$ | 1 | -1 | 1 |
| $\chi^3$ | 2 | 0 | -1 |

Use of character table for analyzing matrix elements:

Suppose that it is necessary to evaluate a matrix element

$$\left\langle \Psi_1 \middle| O \middle| \Psi_2 \right\rangle = \int d^3r \Psi_1^*(\mathbf{r}) O \Psi_2(\mathbf{r})$$

$$= 0 \text{ if } \sum_R \left(\Gamma^i(R)\right)^* \Gamma^j(R)\Gamma^k(R) = 0$$



Matrix element example -- continued

$$\left\langle \Psi_1 \middle| O \middle| \Psi_2 \right\rangle = \int d^3r \Psi_1^*(\mathbf{r}) O \Psi_2(\mathbf{r})$$

$$= 0 \text{ if } \sum_R \left(\Gamma^i(R)\right)^* \Gamma^j(R)\Gamma^k(R) = 0$$

$$\text{or } \sum_e N_e \left(\chi^i(\mathcal{C})\right)^* \chi^j(\mathcal{C})\chi^k(\mathcal{C}) = 0$$

Initial state Operator Final state

Use of character table analysis in crystal field splitting

Question: What happens to a spherical atom when placed in a crystal?

In a spherical environment, an atomic wave function has the form:

$$\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$$

with $m = -l, -l+1, \ldots 0, 1, \ldots, l-1, l \qquad 2l+1$ values

The group which describes the general rotations in 3-dimensions has an infinite number of members, but an important representation of this group is the matrix which rotates to coordinate system about the origin $\mathcal{R}$, transforming $Y_{lm}(\hat{\mathbf{r}}) \rightarrow Y_{lm}(\hat{\mathbf{r}}')$.

It can be shown that: $\mathcal{R}Y_{lm}(\hat{\mathbf{r}}) = \Gamma^{l}_{mm'}(\mathcal{R})Y_{lm'}(\hat{\mathbf{r}})$



Analysis of the 3-dimensional rotation group -- continued

$$\mathcal{R}Y_{lm}(\hat{\mathbf{r}}) = \Gamma^{l}_{mm'}(\mathcal{R})Y_{lm'}(\hat{\mathbf{r}})$$

$$\chi^{l}(\mathcal{R}) = \sum_{m=-l}^{l} \Gamma^{l}_{mm}(\mathcal{R})$$

Note that for $\mathcal{R}$ corresponding to a rotation of $\phi$ about the $\mathbf{z}$ – axis,

$$\Gamma^{l}_{mm'}(\mathcal{R}) = e^{im\phi}\delta_{mm'}$$

$$\Rightarrow \chi^{l}(\mathcal{R}) = \sum_{m=-l}^{l} e^{im\phi} = \frac{\sin\left(\left(l+\frac{1}{2}\right)\phi\right)}{\sin\left(\frac{\phi}{2}\right)}$$

Note that the character for inversion is $\chi^{l}(\mathcal{J}) = (2l+1)(-1)^{l}$

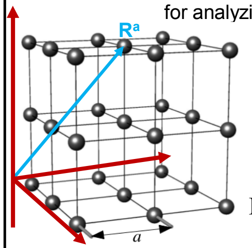
and $\chi^{l}(\mathcal{J}\mathcal{R}) = (-1)^{l}\dfrac{\sin\left(\left(l+\frac{1}{2}\right)\phi\right)}{\sin\left(\frac{\phi}{2}\right)}$



| $\Gamma, R, H$ | $E$ | $3C_4^2$ | $6C_4$ | $6C_2$ | $8C_3$ | $J$ | $3JC_4^2$ | $6JC_4$ | $6JC_2$ | $8JC_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| $\Gamma_2$ | 1 | 1 | −1 | −1 | 1 | 1 | 1 | −1 | −1 | 1 | |
| $\Gamma_{12}$ | 2 | 2 | 0 | 0 | −1 | 2 | 2 | 0 | 0 | −1 | |
| $\Gamma_{15}'$ | 3 | −1 | 1 | −1 | 0 | 3 | −1 | 1 | −1 | 0 | |
| $\Gamma_{25}'$ | 3 | −1 | −1 | 1 | 0 | 3 | −1 | −1 | 1 | 0 | |
| $\Gamma_1'$ | 1 | 1 | 1 | 1 | 1 | −1 | −1 | −1 | −1 | −1 | |
| $\Gamma_2'$ | 1 | 1 | −1 | −1 | 1 | −1 | −1 | 1 | 1 | −1 | |
| $\Gamma_{12}'$ | 2 | 2 | 0 | 0 | −1 | −2 | −2 | 0 | 0 | 1 | |
| $\Gamma_{15}$ | 3 | −1 | 1 | −1 | 0 | −3 | 1 | −1 | 1 | 0 | |
| $\Gamma_{25}$ | 3 | −1 | −1 | 1 | 0 | −3 | 1 | 1 | −1 | 0 | |
| *l*=0 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | $\Gamma_1$ |
| *l*=1 | 3 | -1 | 1 | -1 | 0 | -3 | 1 | -1 | 1 | 0 | $\Gamma_{15}$ |
| *l*=2 | 5 | 1 | -1 | 1 | -1 | 5 | 1 | -1 | 1 | -1 | |

$\Gamma_{12}+\Gamma_{25'}$

## Linear combinations of atomic orbitals (LCAO) methods for analyzing electronic structure




Bloch wave:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

periodic function

Let $\mathbf{R}^a = \boldsymbol{\tau}^a + \mathbf{T}$

basis vector

lattice translation

Bloch wave identity:

$$\Psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\Psi_{n\mathbf{k}}(\mathbf{r})$$

LCAO basis functions with Bloch symmetry:

$$\Phi^{a\,nlm}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^a+\mathbf{T})}\phi^a_{nlm}(\mathbf{r}-\boldsymbol{\tau}^a-\mathbf{T})$$



## LCAO methods -- continued – Slater-Koster analysis

LCAO basis functions with Bloch symmetry:

$$\Phi^{a\,nlm}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^a+\mathbf{T})}\phi^a_{nlm}(\mathbf{r}-\boldsymbol{\tau}^a-\mathbf{T})$$

Approximate Bloch wavefunction:

$$\Psi_{\alpha\mathbf{k}}(\mathbf{r}) = \sum_{a\,nlm} X^{a\,nlm}_{\alpha\mathbf{k}}\Phi^{a\,nlm}_{\mathbf{k}}(\mathbf{r})$$

In this basis, we can estimate the electron energy by variationally computing the expectation value of the Hamiltonian:

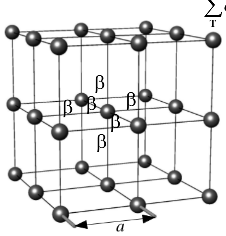
$$E_{\alpha\mathbf{k}} = \frac{\langle\Psi_{\alpha\mathbf{k}}|H|\Psi_{\alpha\mathbf{k}}\rangle}{\langle\Psi_{\alpha\mathbf{k}}|\Psi_{\alpha\mathbf{k}}\rangle}$$

Terms in this expansion have the form:

$$\sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^a-\boldsymbol{\tau}^b+\mathbf{T})}\left\langle\phi^a_{n'l'm'}(\mathbf{r}-\boldsymbol{\tau}^b)\middle|H\middle|\phi^a_{nlm}(\mathbf{r}-\boldsymbol{\tau}^a-\mathbf{T})\right\rangle$$



## Example




Terms in the expansion have the form:

$$\sum_{\mathbf{T}} e^{i\mathbf{k}\cdot(\boldsymbol{\tau}^a-\boldsymbol{\tau}^b+\mathbf{T})}\left\langle\phi^a_{n'l'm'}(\mathbf{r}-\boldsymbol{\tau}^b)\middle|H\middle|\phi^a_{nlm}(\mathbf{r}-\boldsymbol{\tau}^a-\mathbf{T})\right\rangle$$

For nearest neighbor contributions:

$$\left(e^{ik_xa}+e^{-ik_xa}+e^{ik_ya}+e^{-ik_ya}+e^{ik_za}+e^{-ik_za}\right)\beta =$$
$$\left(2\cos(k_xa)+2\cos(k_ya)+2\cos(k_za)\right)\beta$$