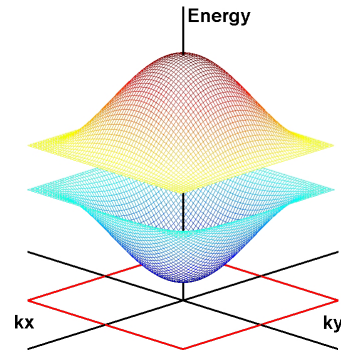
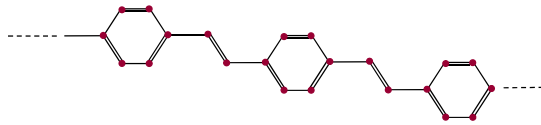


## Handout 10

### The Tight Binding Method (Contd...) And Crystal Symmetries and Energy Bands

In this lecture you will learn:

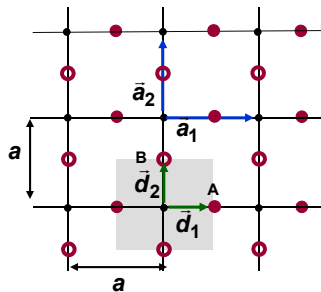
- The tight binding method (contd...)
- The  $\pi$ -bands in conjugated hydrocarbons
- The relationship between symmetries and energy bands



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### Tight Binding for a Square Lattice with a Two-Atom Basis

Consider a 2D square lattice with a two-atom basis:



- The primitive vectors and basis vectors are as follows:

$$\bar{a}_1 = a \hat{x} \quad \bar{a}_2 = a \hat{y}$$

$$\bar{d}_1 = \frac{a}{2} \hat{x} \quad \bar{d}_2 = \frac{a}{2} \hat{y}$$

- Each basis atom contributes one s-orbital that participates in bonding  
 $\Rightarrow$  Each primitive cell contributes two s-orbitals that participate in bonding

$$\phi_{SA}(\vec{r}) \leftrightarrow E_{SA}$$

$$\phi_{SB}(\vec{r}) \leftrightarrow E_{SB}$$

One can write the trial tight-binding solution for wavevector  $\vec{k}$  as:

$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\vec{k} \cdot \vec{R}_m}}{\sqrt{N}} \left[ c_{SA}(\vec{k}) e^{i\vec{k} \cdot \vec{d}_1} \phi_{SA}(\vec{r} - \vec{R}_m - \vec{d}_1) + c_{SB}(\vec{k}) e^{i\vec{k} \cdot \vec{d}_2} \phi_{SB}(\vec{r} - \vec{R}_m - \vec{d}_2) \right]$$

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### Analysis of the Tight Binding Solution

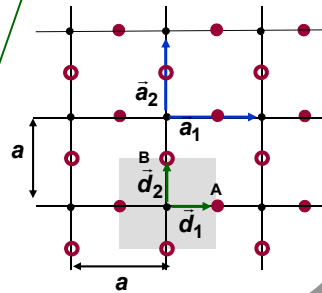
$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\vec{k} \cdot \vec{R}_m}}{\sqrt{N}} \left[ c_{SA}(\vec{k}) e^{i\vec{k} \cdot \vec{d}_1} \phi_{SA}(\vec{r} - \vec{R}_m - \vec{d}_1) + c_{SB}(\vec{k}) e^{i\vec{k} \cdot \vec{d}_2} \phi_{SB}(\vec{r} - \vec{R}_m - \vec{d}_2) \right]$$

(1) Summation over all primitive cells

(2) Common phase factor for each primitive cell

(3) Summation over all orbitals within a primitive cell with undetermined coefficients

(4) A phase factor for each orbital that is related to the position of the orbital within the primitive cell w.r.t. lattice point



### Tight Binding Solution

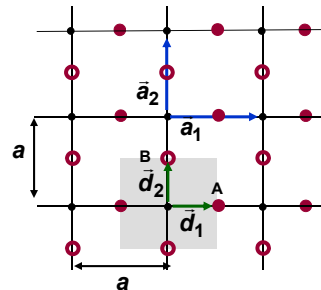
Plug the solution into the Schrodinger equation:  $\hat{H} |\psi_{\vec{k}}(\vec{r})\rangle = E(\vec{k}) |\psi_{\vec{k}}(\vec{r})\rangle$

And then, one by one, multiply by from the left by the bra's corresponding to every orbital in one primitive cell to generate as many equations as the number of orbitals per primitive cell

**Step 1:**

Multiply the equation with  $\langle \phi_{SA}(\vec{r} - \vec{d}_1) |$  and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal



$$E_{SA} c_{SA}(\vec{k}) - 4V_{ss\sigma} \cos(\vec{k} \cdot \vec{d}_1) \cos(\vec{k} \cdot \vec{d}_2) c_{SB}(\vec{k}) = E(\vec{k}) c_{SA}(\vec{k})$$

where the following identity has been used:

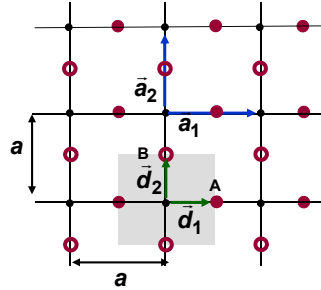
$$e^{i\vec{k} \cdot (\vec{d}_1 + \vec{d}_2)} + e^{i\vec{k} \cdot (\vec{d}_1 - \vec{d}_2)} + e^{i\vec{k} \cdot (-\vec{d}_1 + \vec{d}_2)} + e^{i\vec{k} \cdot (-\vec{d}_1 - \vec{d}_2)} = 4 \cos(\vec{k} \cdot \vec{d}_1) \cos(\vec{k} \cdot \vec{d}_2)$$

## Tight Binding Solution

**Step 2:**

- Multiply the equation with  $\langle \phi_{SB}(\vec{r} - \vec{d}_2) |$  and:
- keep the energy matrix elements for orbitals that are nearest neighbors, and
  - assume that the orbitals on different atoms are orthogonal

$$E_{SB} c_{SB}(\vec{k}) - 4V_{ss\sigma} \cos(\vec{k} \cdot \vec{d}_1) \cos(\vec{k} \cdot \vec{d}_2) c_{SA}(\vec{k}) = E(\vec{k}) c_{SB}(\vec{k})$$

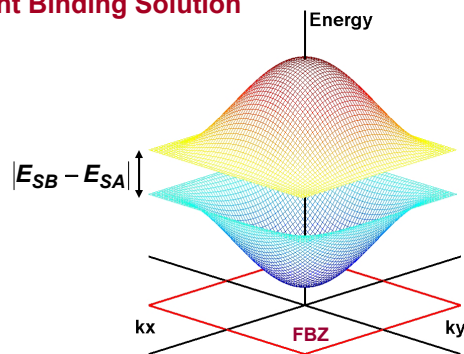
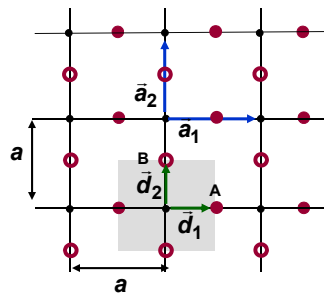


Write the equations obtained in a matrix form:

$$\begin{bmatrix} E_{SA} & -4V_{ss\sigma} \cos(\vec{k} \cdot \vec{d}_1) \cos(\vec{k} \cdot \vec{d}_2) \\ -4V_{ss\sigma} \cos(\vec{k} \cdot \vec{d}_1) \cos(\vec{k} \cdot \vec{d}_2) & E_{SB} \end{bmatrix} \begin{bmatrix} c_{SA}(\vec{k}) \\ c_{SB}(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_{SA}(\vec{k}) \\ c_{SB}(\vec{k}) \end{bmatrix}$$

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## Tight Binding Solution

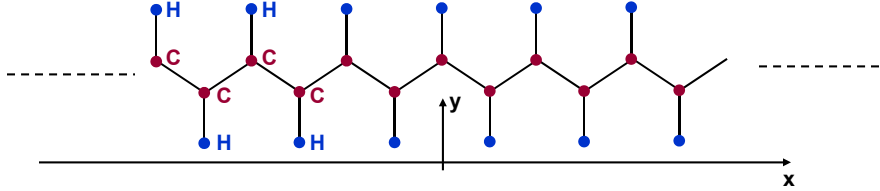


$$\begin{bmatrix} E_{SA} & -4V_{ss\sigma} \cos(\vec{k} \cdot \vec{d}_1) \cos(\vec{k} \cdot \vec{d}_2) \\ -4V_{ss\sigma} \cos(\vec{k} \cdot \vec{d}_1) \cos(\vec{k} \cdot \vec{d}_2) & E_{SB} \end{bmatrix} \begin{bmatrix} c_{SA}(\vec{k}) \\ c_{SB}(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_{SA}(\vec{k}) \\ c_{SB}(\vec{k}) \end{bmatrix}$$

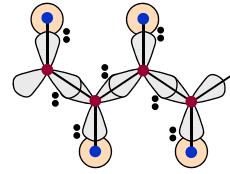
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## Polyacetylene

Polyacetylene is a one-dimensional conducting hydrocarbon polymer

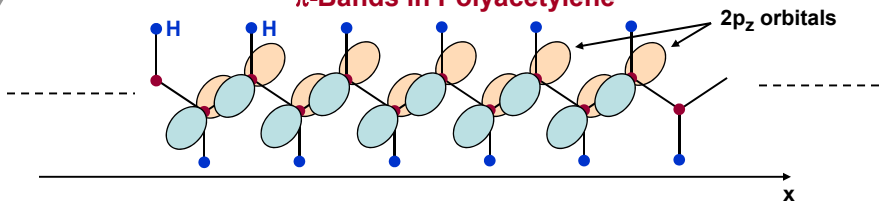


- Carbon atoms are all  $sp^2$  hybridized (one  $2s$  orbital together with the  $2p_x$  and the  $2p_y$  orbitals generate three  $sp^2$  orbitals)
- Two  $sp^2$  orbitals form  $\sigma$ -bonds with the  $sp^2$  orbitals of the neighboring carbon atoms and one remaining  $sp^2$  orbital forms a  $\sigma$ -bond with the  $1s$  orbital of the hydrogen atom
- The bonding orbital associated with each  $\sigma$ -bond is occupied by two electrons (spin-up and spin-down)
- There is one electron per carbon atom left in the  $2p_z$  orbital



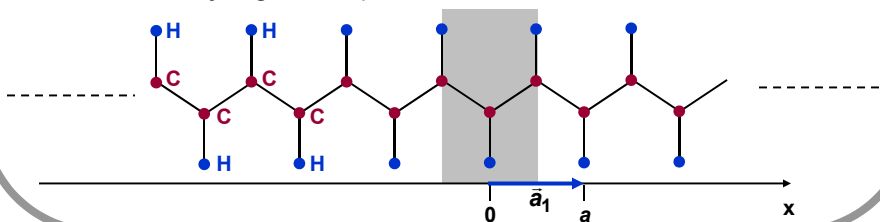
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## $\pi$ -Bands in Polyacetylene



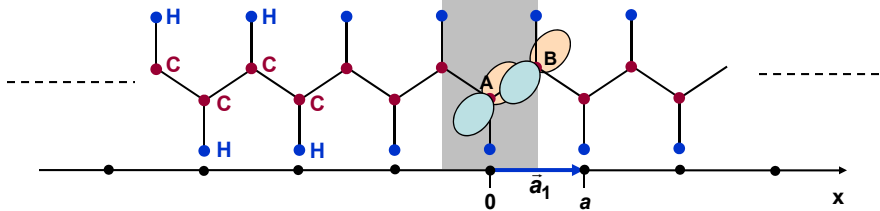
- The  $2p_z$  orbitals stick out of the plane of the chain and form  $\pi$ -bonds with neighboring  $2p_z$  orbitals
- The p-bonding results in energy bands that we will study via tight binding

The primitive cell of the 1D chain is as shown below (it consists of two carbon atoms and two hydrogen atoms)



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### π-Bands in Polyacetylene



Two carbon atoms per primitive cell implies we have a 1D crystal with a two-atom basis with basis vectors:

$$\vec{d}_1 = 0 \quad \vec{d}_2 = \frac{a}{2} \hat{x}$$

- Each basis atom contributes one  $2p_z$ -orbital that participates in bonding
- ⇒ Each primitive cell contributes two  $2p_z$ -orbitals that participate in bonding

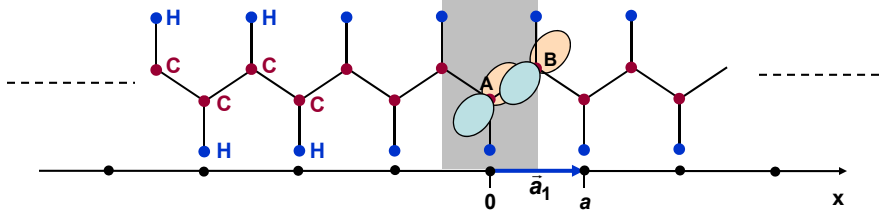
$$\phi_{pzA}(\vec{r}) \leftrightarrow E_p \quad \phi_{pzB}(\vec{r}) \leftrightarrow E_p$$

One can write the trial tight-binding solution for wavevector  $\vec{k}$  as:

$$\psi_{\vec{k}}(\vec{r}) = \sum_m \frac{e^{i\vec{k} \cdot \vec{R}_m}}{\sqrt{N}} \left[ c_{pzA}(\vec{k}) \phi_{pzA}(\vec{r} - \vec{R}_m) + c_{pzB}(\vec{k}) e^{i\vec{k} \cdot \vec{d}_2} \phi_{pzB}(\vec{r} - \vec{R}_m - \vec{d}_2) \right]$$

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### π-Bands in Polyacetylene



Plug the solution into the Schrodinger equation:  $\hat{H} |\psi_{\vec{k}}(\vec{r})\rangle = E(\vec{k}) |\psi_{\vec{k}}(\vec{r})\rangle$

And then, one by one, multiply by from the left by the bra's corresponding to every orbital in one primitive cell to generate as many equations as the number of orbitals per primitive cell

**Step 1:**

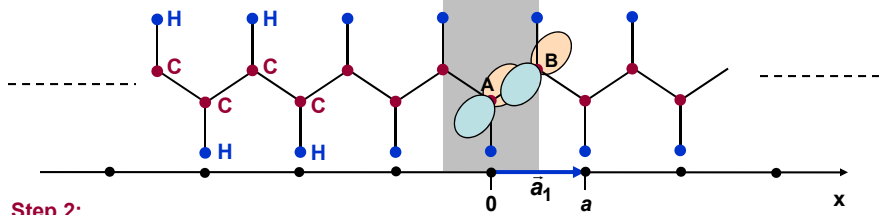
Multiply the equation with  $\langle \phi_{pzA}(\vec{r}) |$  and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

$$E_p c_{pzA}(\vec{k}) - 2V_{pp\pi} \cos(\vec{k} \cdot \vec{d}_2) c_{pzB}(\vec{k}) = E(\vec{k}) c_{pzA}(\vec{k})$$

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### $\pi$ -Bands in Polyacetylene



**Step 2:**

Multiply the equation with  $\langle \phi_{pzB}(\vec{r}) |$  and:

- keep the energy matrix elements for orbitals that are nearest neighbors, and
- assume that the orbitals on different atoms are orthogonal

$$E_p c_{pzB}(\vec{k}) - 2V_{pp\pi} \cos(\vec{k} \cdot \vec{d}_2) c_{pzA}(\vec{k}) = E(\vec{k}) c_{pzB}(\vec{k})$$

Write the equations obtained in a matrix form:

$$\begin{bmatrix} E_p & -2V_{pp\pi} \cos(\vec{k} \cdot \vec{d}_2) \\ -2V_{pp\pi} \cos(\vec{k} \cdot \vec{d}_2) & E_p \end{bmatrix} \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}$$

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### $\pi$ -Bands in Polyacetylene

$$\begin{bmatrix} E_p & -2V_{pp\pi} \cos(\vec{k} \cdot \vec{d}_2) \\ -2V_{pp\pi} \cos(\vec{k} \cdot \vec{d}_2) & E_p \end{bmatrix} \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix} = E(\vec{k}) \begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}$$

**Solutions are:**

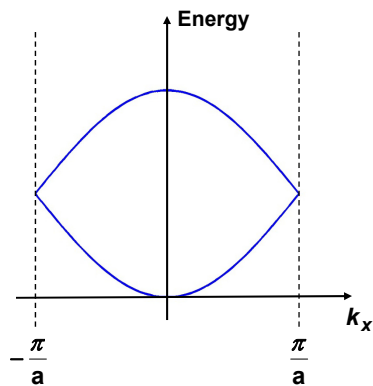
$$E(\vec{k}) = E_p \pm 2V_{pp\pi} |\cos(\vec{k} \cdot \vec{d}_2)|$$

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_+ = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

$$\begin{bmatrix} c_{pzA}(\vec{k}) \\ c_{pzB}(\vec{k}) \end{bmatrix}_- = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

- There is no bandgap between the upper and lower bands!

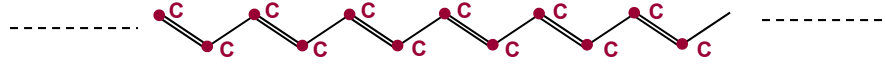
- Since each primitive cell contributes two electrons, the lower band is completely filled and the upper band is completely empty at  $T=0K$



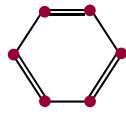
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### Other Conducting $\pi$ -Conjugated Molecules and Polymers

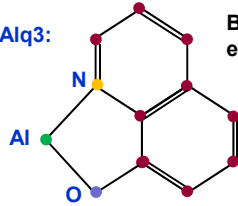
**Polyacetylene:**



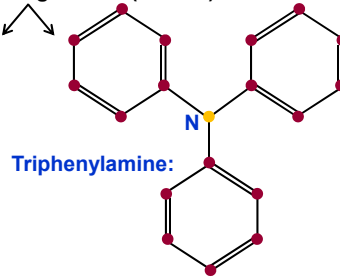
**Benzene:**



**Alq3:**

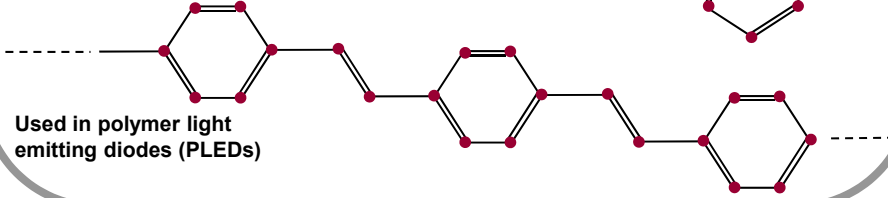


Both used in organic light emitting diodes (OLEDs)



**Triphenylamine:**

**PPV (Polyphenylene Vinylene):**



Used in polymer light emitting diodes (PLEDs)

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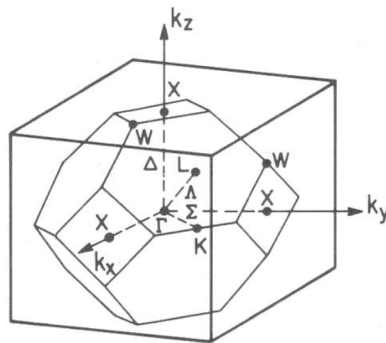
### Tight Binding Bands For Germanium

**Germanium:**

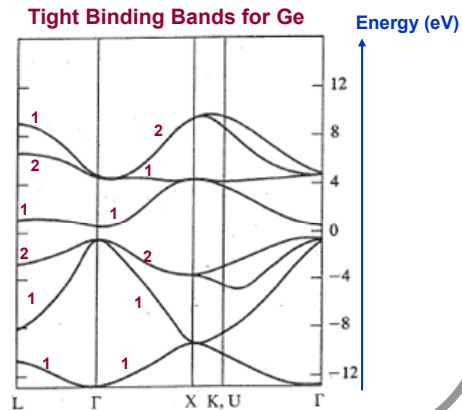
**Atomic number: 32**

**Electron Configuration:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$**

**Number of electrons in the outermost shell: 4**



**FBZ (for FCC lattice)**



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### Symmetry and Energy Bands

The crystal potential  $V(\vec{r})$  generally has certain other symmetries in addition to the lattice translation symmetry:

$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

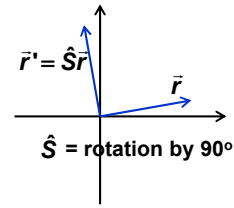
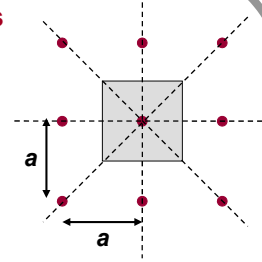
For example, the 2D potential of a square atomic lattice, as shown, has the following symmetries:

- Symmetry under rotations by 90, 180, and 270 degrees
- Symmetry under reflections w.r.t. x-axis and y-axis
- Symmetry under reflections w.r.t. the two diagonals

Let  $\hat{S}$  be the operator (in matrix representation) for any one of these symmetry operations then:

$$\vec{r}' = \hat{S}\vec{r}$$

$$\Rightarrow V(\hat{S}\vec{r}) = V(\vec{r})$$



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### Crystal Point-Group Symmetry

#### Point-Group Symmetry

The point group symmetry operation of a lattice are all those operations that leave the lattice unchanged and at least one point of the lattice remains unmoved under the operation

Point group symmetry operations can include:

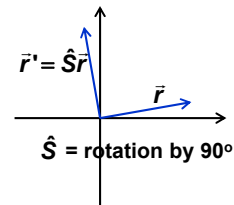
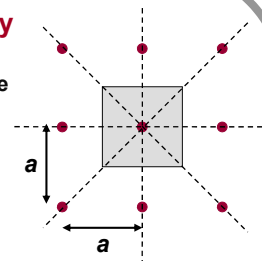
- Rotations (w.r.t. to axes of rotation)
- Reflections (across lines or planes)
- Inversions (w.r.t. to a point)

Let  $\hat{S}$  be the operator for a point-group symmetry operation, such that:

$$V(\hat{S}\vec{r}) = V(\vec{r})$$

The operator  $\hat{S}$  is unitary:

$$\hat{S}^T = \hat{S}^{-1} \Rightarrow \text{unitary}$$



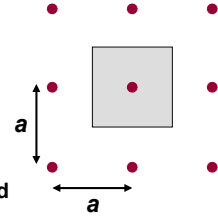
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### Crystal Point-Group Symmetry and Energy Bands

Let  $\hat{S}$  be the operator for a point-group symmetry operation, such that:

$$\begin{aligned} \vec{r}' &= \hat{S}\vec{r} & \left\{ \hat{S}^T = \hat{S}^{-1} \Rightarrow \text{unitary} \right. \\ \Rightarrow V(\hat{S}\vec{r}) &= V(\vec{r}) \end{aligned}$$



Suppose one has solved the Shrodinger equation and obtained the energy and wavefunction of a Bloch State  $\psi_{n,\vec{k}}(\vec{r})$

$$\left[ -\frac{\hbar^2 \nabla_{\vec{r}}^2}{2m} + V(\vec{r}) \right] \psi_{n,\vec{k}}(\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}(\vec{r})$$

Now replace  $\vec{r}$  by  $\hat{S}\vec{r}$  everywhere in the Schrodinger equation:

$$\begin{aligned} \left[ -\frac{\hbar^2 \nabla_{\hat{S}\vec{r}}^2}{2m} + V(\hat{S}\vec{r}) \right] \psi_{n,\vec{k}}(\hat{S}\vec{r}) &= E_n(\vec{k}) \psi_{n,\vec{k}}(\hat{S}\vec{r}) & \longrightarrow & \left\{ \begin{array}{l} \nabla_{\hat{S}\vec{r}}^2 = \nabla_{\vec{r}}^2 \\ \text{Laplacian is invariant} \end{array} \right. \\ \Rightarrow \left[ -\frac{\hbar^2 \nabla_{\vec{r}}^2}{2m} + V(\vec{r}) \right] \psi_{n,\vec{k}}(\hat{S}\vec{r}) &= E_n(\vec{k}) \psi_{n,\vec{k}}(\hat{S}\vec{r}) \end{aligned}$$

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### Crystal Point-Group Symmetry and Energy Bands

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\hat{S}\vec{r}) \right] \psi_{n,\vec{k}}(\hat{S}\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}(\hat{S}\vec{r}) \Rightarrow \left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_{n,\vec{k}}(\hat{S}\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}(\hat{S}\vec{r})$$

The above equation says that the function  $\psi_{n,\vec{k}}(\hat{S}\vec{r})$  is also a Bloch state with the same energy as  $\psi_{n,\vec{k}}(\vec{r})$  (we have found a new eigenfunction!)

The question is if we really have found a new eigenfunction or not, and if so what is the wavevector of this new eigenfunction

We know that Bloch functions have the property that:  $\psi_{n,\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{n,\vec{k}}(\vec{r})$

So we try this on  $\psi_{n,\vec{k}}(\hat{S}\vec{r})$ :

$$\begin{aligned} \psi_{n,\vec{k}}(\hat{S}(\vec{r} + \vec{R})) &= \psi_{n,\vec{k}}(\hat{S}\vec{r} + \hat{S}\vec{R}) & \longrightarrow & \left\{ \begin{array}{l} \hat{S}\vec{R} \text{ is also a lattice vector} \\ \vec{k} \cdot (\hat{S}\vec{R}) = (\hat{S}^{-1}\vec{k}) \cdot \vec{R} \end{array} \right. \\ &= e^{i\vec{k} \cdot \hat{S}\vec{R}} \psi_{n,\vec{k}}(\hat{S}\vec{r}) = e^{i[\hat{S}^{-1}\vec{k}] \cdot \vec{R}} \psi_{n,\vec{k}}(\hat{S}\vec{r}) \end{aligned}$$

$\Rightarrow \psi_{n,\vec{k}}(\hat{S}\vec{r})$  is a Bloch function with wavevector  $\hat{S}^{-1}\vec{k}$  and energy  $E_n(\vec{k})$

$\Rightarrow \psi_{n,\vec{k}}(\hat{S}\vec{r}) = \psi_{n,\hat{S}^{-1}\vec{k}}(\vec{r})$

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### Crystal Point-Group Symmetry and Energy Bands

So we finally have for the symmetry operation  $\hat{S}$  :

$$\Rightarrow \psi_{n,\bar{k}}(\hat{S}\vec{r}) = \psi_{n,\hat{S}^{-1}\bar{k}}(\vec{r})$$

We also know that the eigenenergy of  $\psi_{n,\hat{S}^{-1}\bar{k}}(\vec{r})$  is  $E_n(\bar{k})$

Therefore:

$$E_n(\hat{S}^{-1}\bar{k}) = E_n(\bar{k})$$

Or, equivalently:

$$E_n(\hat{S}\bar{k}) = E_n(\bar{k})$$

#### Important Lessons:

1) If  $\hat{S}$  is a symmetry of the potential such that in real-space we have:

$$V(\hat{S}\vec{r}) = V(\vec{r})$$

then the energy bands also enjoy the symmetry of the potential such that in k-space:

$$E_n(\hat{S}\bar{k}) = E_n(\bar{k})$$

2) Degeneracies in the energy bands can therefore arise from crystal point-group symmetries!

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### Time Reversal Symmetry and Energy Bands

Suppose we have solved the time dependent Schrodinger and obtained the Bloch state  $\psi_{n,\bar{k}}(\vec{r})$  with energy  $E_n(\bar{k})$  :

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_{n,\bar{k}}(\vec{r}, t) = i\hbar \frac{\partial \psi_{n,\bar{k}}(\vec{r}, t)}{\partial t} \quad \longrightarrow \quad \psi_{n,\bar{k}}(\vec{r}, t) = \psi_{n,\bar{k}}(\vec{r}) e^{-i \frac{E_n(\bar{k})}{\hbar} t}$$

After plugging the solution in the time-dependent equation, we get:

$$\left[ -\frac{\hbar^2 \nabla_{\vec{r}}^2}{2m} + V(\vec{r}) \right] \psi_{n,\bar{k}}(\vec{r}) = E_n(\bar{k}) \psi_{n,\bar{k}}(\vec{r})$$

If we take the complex conjugate of the above equation, we get:

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_{n,\bar{k}}^*(\vec{r}) = E_n(\bar{k}) \psi_{n,\bar{k}}^*(\vec{r})$$

We have found another Bloch function, i.e.  $\psi_{n,\bar{k}}^*(\vec{r})$  , with the same energy as  $\psi_{n,\bar{k}}(\vec{r})$

**Question:** What is the physical significance of the state  $\psi_{n,\bar{k}}^*(\vec{r})$  ?

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### Time Reversal Symmetry and Energy Bands

Suppose we have solved the time dependent Schrodinger and obtained the Bloch state  $\psi_{n,\vec{k}}(\vec{r})$  with energy  $E_n(\vec{k})$  :

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_{n,\vec{k}}(\vec{r}, t) = i\hbar \frac{\partial \psi_{n,\vec{k}}(\vec{r}, t)}{\partial t} \longrightarrow \psi_{n,\vec{k}}(\vec{r}, t) = \psi_{n,\vec{k}}(\vec{r}) e^{-i \frac{E_n(\vec{k})}{\hbar} t}$$

Lets see if we can find a solution under **time-reversal** (i.e. when  $t$  is replaced by  $-t$ ):

$$\Rightarrow \left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_{n,\vec{k}}(\vec{r}, -t) = -i\hbar \frac{\partial \psi_{n,\vec{k}}(\vec{r}, -t)}{\partial t}$$

The above does not look like a Schrodinger equation so we complex conjugate it:

$$\Rightarrow \left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_{n,\vec{k}}^*(\vec{r}, -t) = i\hbar \frac{\partial \psi_{n,\vec{k}}^*(\vec{r}, -t)}{\partial t}$$

This means that  $\psi_{n,\vec{k}}^*(\vec{r}, -t)$  is the time-reversed state corresponding to the state  $\psi_{n,\vec{k}}(\vec{r}, t)$

$$\psi_{n,\vec{k}}^*(\vec{r}, -t) = \psi_{n,\vec{k}}^*(\vec{r}) e^{-i \frac{E_n(\vec{k})}{\hbar} t} \longrightarrow \left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_{n,\vec{k}}^*(\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}^*(\vec{r})$$

The function  $\psi_{n,\vec{k}}^*(\vec{r})$  is the time-reversed Bloch state corresponding to  $\psi_{n,\vec{k}}(\vec{r})$

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$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right] \psi_{n,\vec{k}}^*(\vec{r}) = E_n(\vec{k}) \psi_{n,\vec{k}}^*(\vec{r})$$

We have found another Bloch function, i.e.  $\psi_{n,\vec{k}}^*(\vec{r})$ , with the same energy as  $\psi_{n,\vec{k}}(\vec{r})$

The question is if we really have found a new eigenfunction or not, and if so what is the wavevector of this new eigenfunction

We know that Bloch functions have the property that:  $\psi_{n,\vec{k}}(\vec{r} + \vec{R}) = e^{i \vec{k} \cdot \vec{R}} \psi_{n,\vec{k}}(\vec{r})$

So we try this on  $\psi_{n,\vec{k}}^*(\vec{r})$ :

$$\begin{aligned} \psi_{n,\vec{k}}^*(\vec{r} + \vec{R}) &= [\psi_{n,\vec{k}}(\vec{r} + \vec{R})]^* = [e^{i \vec{k} \cdot \vec{R}} \psi_{n,\vec{k}}(\vec{r})]^* = e^{i [-\vec{k}] \cdot \vec{R}} \psi_{n,\vec{k}}^*(\vec{r}) \\ \Rightarrow \psi_{n,\vec{k}}^*(\vec{r}) &\text{ is a Bloch function with wavevector } -\vec{k} \text{ and energy } E_n(\vec{k}) \\ \Rightarrow \psi_{n,-\vec{k}}(\vec{r}) &= \psi_{n,\vec{k}}^*(\vec{r}) \text{ and } E_n(-\vec{k}) = E_n(\vec{k}) \end{aligned}$$

#### Important Lesson:

Time reversal symmetry implies that  $E_n(-\vec{k}) = E_n(\vec{k})$  even if the crystal lacks spatial inversion symmetry (e.g. GaAs, InP, etc)

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