Electronic States in a Crystal

\( \sim 10^{23} \) interacting electrons and ion cores – a big computational problem.

\[
H_T = \left( \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right) + \left( \sum_n \frac{p_n^2}{2M_n} + \frac{1}{2} \sum_{n,n'} \frac{Z_n Z_{n'} e^2}{|\mathbf{R}_n - \mathbf{R}_{n'}|} \right) + \left( -\sum_{n,i} \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|} \right) + H_{\text{spin-orbit-interaction}} + \ldots = H_{el} + H_{\text{core}} + H_{el-core} + H_{\text{soi}} + \ldots
\]

Frozen core approximation: cores at equilibrium positions; no phonons; no electron-phonon interactions, etc.

Ignore spin-orbit-interaction.

\( H_T = H_{el} + H_{el-core} \), still cannot be solved exactly even for two electrons because of cross terms.

Independent \( e^- \) approximation: assuming \( H_T = \sum_i H_i \) (no cross terms), and \( H_i = H \) independent of \( i \) (all electrons treated equally). A good approximation if \( H_i = H \) is chosen wisely.

One electron problem (single-particle approximation):
\[ H = -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \quad \text{\( U = \text{crystal potential} \)} \]

Hartree approx: \( U(\mathbf{r}) = \text{potential from ion cores} + \text{average potential from all other electrons} \)

Hartree-Fock approx \( U(\mathbf{r}) = U_{\text{Hartree}} + U_{\text{exchange}} \) (exchange from exclusion principle)

Generally, \( U(\mathbf{r}) = U_{\text{Hartree}} + U_{\text{exchange}} + U_{\text{correlation}} \) (correlation = whatever is left)

For now, consider \( U \) as given (as a parameterized function).

Translational symmetry: \( U(\mathbf{r}) = U(\mathbf{r} + \mathbf{R}) \)

**Bloch theorem:** wave function is of the form \( \psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_k(\mathbf{r}) \),

where \( u_k(\mathbf{r}) = u_k(\mathbf{r} + \mathbf{R}) \) = a periodic function.

\( \mathbf{k} = \text{wave vector} = \text{quantum number related to translation} \)

\( \hbar \mathbf{k} \equiv \text{crystal momentum} \)
Translating the wave function by $R$: $\psi(r + R) = e^{i\mathbf{k} \cdot (r + R)} u_k(r + R)$

Equivalent form of Bloch theorem

$$\psi(r + R) = e^{i\mathbf{k} \cdot R} \psi(r)$$

Proof: Define translation operator $T(R)\psi(r) = \psi(r + R)$.

Explicit form of $T(R)$ from Taylor expansion:

$$\psi(r + R) = \sum_{n=0}^{\infty} \frac{1}{n!} (\mathbf{R} \cdot \nabla)^n \psi(r) = \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{\mathbf{R} \cdot \mathbf{p}}{-i\hbar} \right)^n \psi(r) = \exp\left( i\mathbf{R} \cdot \frac{\mathbf{p}}{\hbar} \right) \psi(r)$$

So, $T(R) = \exp\left( i\mathbf{R} \cdot \frac{\mathbf{p}}{\hbar} \right)$

Translation symmetry: $H(r + R) = T(R)H(r)T^{-1}(R) = H(r)$; $[T(R), H] = 0$.

Also, $[T(R), T(R')] = 0$.

$H$ and all $T(R)$ form a commuting set.

Can choose $\psi$ to be a simultaneous eigenfunction.

$$H\psi = \varepsilon\psi; T(R)\psi = c(R)\psi.$$
Since $T(R)T(R') = T(R+R')$, $c(R)c(R') = c(R+R')$.

Let $c(a_i) = e^{2\pi i x_i}$; $x_i = \text{complex in general}; \; i = 1, 2, 3$.

$$c(R) = c\left(\sum_i n_i a_i\right) = (e^{2\pi i x_1})^{n_1} (e^{2\pi i x_2})^{n_2} (e^{2\pi i x_3})^{n_3} = e^{i2\pi(n_1 x_1 + n_2 x_2 + n_3 x_3)}$$

Let $k = \sum_i x_i b_j \quad c(R) = e^{k \cdot R} \quad T(R)\psi(r) = \psi(r+R) = e^{i k \cdot R} \psi(r)$. QED

Note $k$ is complex in general.

Alternate proof based on group theory: $T(R)$ form a 3d cyclic group of $\infty$ order. All representations are 1d. Choose the 1d matrix to be $c(a_i) = e^{2\pi i x_i}$. Etc.

Another quick proof:

Because of translation symmetry, if $\psi(r)$ is a solution, $\psi(r+R)$ is also a solution. Choose the basis set such that $\psi(r+R) = c(R)\psi(r)$.

Combining translations, $c(R)c(R') = c(R+R')$.

Let $c(a_i) = e^{2\pi i x_i}; \; x_i = \text{complex in general}; \; i = 1, 2, 3$. 

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\[ c(R) = c \left( \sum_i n_i a_i \right) = \left( e^{2\pi i x_1} \right)^{n_1} \left( e^{2\pi i x_2} \right)^{n_2} \left( e^{2\pi i x_3} \right)^{n_3} = e^{i2\pi (n_1 x_1 + n_2 x_2 + n_3 x_3)} \]

Let \( k = \sum_i x_i b_i \) \[ c(R) = e^{i k \cdot R} \quad \psi(R + R) = e^{i k \cdot R} \psi(R) \]. QED

Again, \( k \) can be complex.

Now, label \( \psi \) using quantum number \( k \) to specify its translational property:

\[ \psi_k(r + R) = e^{i k \cdot R} \psi_k(r) \]

<table>
<thead>
<tr>
<th>Hydrogen atom</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotational symmetry</td>
<td>Translational symmetry ( {R} )</td>
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<td>( H, L^2, L_z )</td>
<td>( H, T(R) )</td>
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<td>( L^2 \psi = \ell(\ell + 1) \hbar^2 \psi )</td>
<td>( T(R)\psi = e^{i k \cdot R} \psi )</td>
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<td>( L_z \psi = m\hbar \psi )</td>
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<td>( \psi_{\ell m} )</td>
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<td>( \psi_{n \ell m}, n = \text{principal quantum number} )</td>
<td>( \psi_{nk}, n = \text{band index} )</td>
</tr>
<tr>
<td>Add spin.</td>
<td>Add spin.</td>
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For mathematical reasons, consider finite crystals with \( N = N_1 \times N_2 \times N_3 \) unit cells.
**Periodic boundary condition** (Born von Karman):

\[ \psi_k (\mathbf{r} + N_i \mathbf{a}_i) = \psi_k (\mathbf{r}) = e^{i\mathbf{k} \cdot N_i \mathbf{a}_i} \psi_k (\mathbf{r}), \quad i = 1, 2, 3. \]

\[ e^{i \mathbf{k} \cdot N_i \mathbf{a}_i} = 1. \]

Let \( \mathbf{k} = \sum_i x_i \mathbf{b}_i \).

\[ e^{i 2\pi x_i N_i} = 1 \quad x_i = \frac{m_i}{N_i}, \text{ where } m_i = \text{integer}. \]

\[ \mathbf{k} = \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3 = \text{allowed values of } \mathbf{k} = \text{real}. \]

(\( \mathbf{k} = \text{complex for surface states, impurity states, etc. with their different boundary conditions.} \))

Consider a unit cell in reciprocal space

\( \mathbf{k} \) is within unit cell if \( 0 \leq m_i \leq N_i \)

**Theorem:**

\( N = \# \text{ of unit cells in real space} = \# \text{ of allowed } \mathbf{k} \text{ values in a reciprocal unit cell} = \# \text{ of allowed } \mathbf{k} \text{ values in the 1}\text{st BZ} \)

Volume per \( \mathbf{k} \) point

\[ = \frac{\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3}{N_1 N_2 N_3} = \frac{1}{N} \frac{8\pi^3}{V} = \frac{8\pi^3}{V}. \]
Density of $k$ points $= \frac{V}{8\pi^3}$: 
\[ \sum_k \rightarrow \frac{V}{8\pi^3} \int d^3k \]
\[ \sum_{k,s} \rightarrow \frac{2V}{8\pi^3} \int d^3k \]

Same as the free electron case (but the axes are not necessarily orthonormal).

**Theorem:** $k$ and $k + K$ ($K$ an arbitrary reciprocal lattice vector) specify the same translation symmetry.

**Proof:** $\psi_k = u_k(r) e^{ik \cdot r} = (u_k(r) e^{-iK \cdot r}) e^{i(k+K) \cdot r} = (\text{periodic function}) \times (\text{phase factor})$

$e^{-iK \cdot r}$ = periodic, because $e^{iK \cdot R} = 1$.

$(u_k(r) e^{-iK \cdot r}) e^{i(k+K) \cdot r}$ is of the Bloch form. Could label $\psi$ with $k + K$ instead of $k$.

QED

To eliminate confusion, **reduced zone scheme** is commonly employed: choose $k$ in the 1st BZ, and then each $k$ is unique; only $N$ distinct $k$’s.

$k = k_{\text{red}} + K$ any wave vector can be reduced to the 1st BZ.

Different states at the same $k$ are labeled (distinguished) by the band index $n$. 
**Band Structure**

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + U \right) \psi_k = \varepsilon_k \psi_k; \quad \psi_k = e^{ik \cdot r} u_k (r).
\]

\[-\frac{\hbar^2}{2m} \left[ \nabla^2 + 2i \mathbf{k} \cdot \nabla - k^2 \right] u_k + U(r) u_k = \varepsilon_k u_k\]

\[H_k u_k = \varepsilon_k u_k; \quad H_k = \text{effective Hamiltonian for } u_k.\]

\[\mathbf{k} = \text{(continuous) parameter.}\]

Given \(\mathbf{k}\), the equation yields solutions with discrete eigenvalues (like the H-atom problem); label them by \(n = \text{band index.}\)

\[H_k u_{nk} = \varepsilon_{nk} u_{nk}\]

**Theorem:** Since \(H_k\) is a smooth function of \(\mathbf{k}\), \(\varepsilon_{nk} = \varepsilon_n (\mathbf{k})\) is a smooth function of \(\mathbf{k}\) for a given \(n\). The allowed solutions form a band.

1d example: \(k = \frac{m}{N} b = \frac{m}{N} \frac{2\pi}{a}\). Reduced zone (1st zone): \(-\frac{N}{2} < m \leq \frac{N}{2}\)
\( N \) distinct \( k \) points in 1\(^{st}\) BZ; \( N \) solutions in each band. As \( N \to \infty \), the resulting band dispersion relation is a smooth curve.

Simplified schematic band diagram:

**Energy gaps** come from the crystal potential. No such gaps for jellium (free electron gas). Propagating states do not exist in gaps.
Consider a solid-solid junction; an incident electron with energy in the gap is simply reflected. Non-propagating states (with complex $k$) can exist in gaps (they are not bulk band structure solutions because they do not satisfy the assumed PBC).

1d example: complex $k = i|k|$: \[ u_k(x) \, e^{ikx} = u_k(x) \, e^{-|k|x} = \text{decaying wave} \]

**1d Kronig-Penny model** (linear array of delta functions)

\[ U(x) = aV \sum_{n=-N/2}^{N/2} \delta(x-na), \text{ with } V > 0. \]

Plane wave solutions in regions 1 and 2:

\[ \psi_{1,2} = A_{1,2} \, e^{ik_0x} + B_{1,2} \, e^{-ik_0x}; \quad k_0 = \frac{\sqrt{2m\varepsilon}}{\hbar} \]

1\textsuperscript{st} BC at origin:

\[ \psi_1(0) = \psi_2(0), \quad A_1 + B_1 = A_2 + B_2 \quad (a) \]

2\textsuperscript{nd} BC at origin:

Crystal potential approximated by $\delta$-functions
Integrate \( -\frac{\hbar^2}{2m} \nabla^2 + aV \sum \delta (x - na) \) \( \psi = \varepsilon \psi \) from 0\(^-\) to 0\(^+\) (can't use continuity of derivative because of the delta function).

\[-\frac{\hbar^2}{2m} \left[ \psi'(0^+) - \psi'(0^-) \right] + aV \psi(0) = 0\]

\[-\frac{i\hbar^2 k_0}{2m} \left( A_2 - B_2 - A_1 + B_1 \right) + aV (A_1 + B_1) = 0 \]  \hspace{1cm} (b)

Bloch theorem: \( \psi_2(a^-) = e^{ika} \psi_1(0^-); \quad \psi_2'(a^-) = e^{ika} \psi_1'(0^-) \)

\[ A_2 e^{ika} + B_2 e^{-ika} = e^{ika} (A_1 + B_1) \]  \hspace{1cm} (c)

\[ A_2 e^{ika} - B_2 e^{-ika} = e^{ika} (A_1 - B_1) \]  \hspace{1cm} (d)

(a)-(d): 4 equations for 4 unknowns; secular equation; determinant = 0; etc.

\[
\cos(ka) = \cos(k_0 a) + \frac{Vma^2}{\hbar^2} \sin k_0 a \quad \text{with} \quad k_0 = \frac{\sqrt{2m\varepsilon}}{\hbar} ; \quad \text{an implicit equation for} \quad \varepsilon(k).
\]

Define \( P = \frac{Vma^2}{\hbar^2} ; \quad \alpha^2 = k_0^2 a^2 = \frac{2m\varepsilon}{\hbar^2} a^2 \)
\[ f(\alpha) = \cos \alpha + \frac{P \sin \alpha}{\alpha}; \quad f(\alpha) = \cos(ka) \]

If \( |f(\alpha)| \leq 1 \), a solution exists for each \( k \); if \( |f(\alpha)| > 1 \), there is no solution for real \( k \).

Example, \( P = 1 \).

Allowed propagating states form bands. Each band spans \(-1 \leq \cos ka \leq 1\),

or, \(-\frac{\pi}{a} < k \leq \frac{\pi}{a}\) \( (1^{st} \text{ BZ}) \).
Resulting band structure is consistent with expectation based on general considerations.

When \( \varepsilon \to \infty \), \( f(\alpha) \sim \cos \alpha = \cos(ka) \),
\( \alpha = ka + 2\ell \pi \), where \( \ell \) = integer.

\[
\sqrt{\frac{2m\varepsilon}{h^2}} = k + \frac{2\ell \pi}{a}
\]

So,
\[
\varepsilon_n = \frac{\hbar^2}{2m} \left( k + \frac{2\pi \ell}{a} \right)^2 = \frac{\hbar^2}{2m} (k + K)^2 = \frac{\hbar^2}{2m} \kappa'^2,
\]
which is just the free electron result. \( \kappa' \) is wave vector in "extended zone".

At high energies, crystal potential becomes less important; band structure approaches free electron results.

1-D free electron model

\[
\psi \propto e^{ikx}; \quad \varepsilon(k) = \frac{\hbar^2 k^2}{2m}
\]

\[
e^{ikx} = e^{i(k_1 + K)x} = e^{ik_1 x}e^{iKx} = e^{ik_{1x}}u(x) \quad \text{in Bloch form, where } k_1 \text{ is in 1}^{\text{st}} \text{ BZ.}
\]
\[ \varepsilon(k) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left( k_1 + K \right)^2 = \frac{\hbar^2}{2m} \left( k_1 + \frac{2\pi \ell}{a} \right)^2, \] where \( \ell = \text{integer} \).

Relabel bands: \( \varepsilon_{\ell}(k_1) \), where \( \ell = \) some kind of quantum number, related to band index \( n \).
Adding a crystal potential (as in the KP model), gaps are formed.
3d band structure: \( \varepsilon_n(k) \) = a continuous function of \( k \) for given \( n \), with possibly complex shapes. Usually plot \( \varepsilon_n(k) \) along a few high symmetry lines in the 1\textsuperscript{st} BZ.

Example: Si band structure (fcc)
Given \( n \), there are \( N \) solutions \( \psi_{nk} \) corresponding to \( N \) different \( k \)'s in 1\textsuperscript{st} BZ.

**Theorem**: each band can accommodate \( 2N \) electrons (2 from spin).

A solid has \( N \left( \sum_{\alpha} Z_\alpha \right) \) electrons, where \( \sum_{\alpha} Z_\alpha = \text{total valence/cell} \).

For Si, valence = 4, \( \sum_{\alpha} Z_\alpha = 8 \) (2 atoms per unit cell).

For GaAs, valence of Ga = 3; valence of As = 5; \( \sum_{\alpha} Z_\alpha = 8 \), also.

In each case, \( 8N \) electrons total; filling 4 bands exactly.

Ground state of Si and GaAs: \( n = 1, 2, 3, \) and 4 are filled; \( n = 5, \ldots \) are empty.

Energy gap (band gap, fundamental gap) \( \sim 1.1 \) eV for Si, 1.5 eV for GaAs.

This gap is responsible for semiconducting behavior (requires finite energy to excite carriers).

For comparison: jellium model always yields metals (no gaps).
A filled band in an electric field $E$ along $-x$:

As will show later, Newton's equation is still OK.

$$\hbar \frac{dk}{dt} = -eE; \quad k = \frac{-eE}{\hbar} t.$$ 

All electrons move together. One by one, they hit the ZB and return (umklapp) to the other side of the BZ. The band is always filled. Electric current from $+k$ and $-k$ states cancel. No net current. Scattering does not change things. Filled bands $\Rightarrow$ **Insulator**.

A partially filled band and an $E$ field:

$$\hbar \frac{dk}{dt} + \frac{\hbar k}{\tau} = -eE; \quad \langle k \rangle = \frac{-eE \tau}{\hbar}$$

Unbalanced distribution. A net current. Partially filled bands $\Rightarrow$ **Conductor (metal)**.
Carriers can be excited thermally at finite temperatures. Conductivity determined by carrier density. The larger the gap is, the more insulating.

Typically, a material is considered an insulator if gap > 4 or 5 eV. Otherwise, semiconductors.

**Theorem:** \( \sum_{\alpha} Z_\alpha = \text{odd} \Rightarrow \text{metal} \), because there is at least one partially filled band.
Insulators & semiconductors $\Rightarrow \sum_{\alpha} Z_{\alpha} =$ even (in order to have a gap).

However, $\sum_{\alpha} Z_{\alpha} =$ even $\Rightarrow$ an insulator/semiconductor or a metal (due to band overlap).

Examples:

Alkali metals (Li, Na, K, Rb, Cs), $\sum_{\alpha} Z_{\alpha} = 1$. The lowest band is exactly half filled. Each is a metal.

He, $\sum_{\alpha} Z_{\alpha} = 2$, a quantum solid (under $p$ at very low $T$).

Be, Mg, … $\sum_{\alpha} Z_{\alpha} = 2$. These are metals because of band overlap.

Al, Ga, In, …, $\sum_{\alpha} Z_{\alpha} = 3$, metals.
Si, Ge, diamond, $\sum Z_\alpha = 8$ (2 atoms per unit cell), 4 filled bands, semiconductors (or insulators).

Semimetals – very small band overlaps at $E_F$, such as Bi and graphite.

**Symmetry Properties of Band Structure**

**Translation symmetry** –

$\psi_k$ can be written as $\psi_{k+K}$, $K$ = arbitrary reciprocal lattice vector

So, $\psi_{n,k} = \psi_{n,k+K}$ and $\varepsilon_n(k) = \varepsilon_n(k + K)$.

**Repeated zone scheme**: $\varepsilon_n(k)$ is periodic in reciprocal space.

For comparison: **reduced zone scheme**, where only the 1st zone is considered.

**Point group symmetry operations**:

1d: consider a 1d crystal with a monatomic basis (1 atom per unit cell).
The system is symmetric with respect to reflection about the origin (or inversion).

1. \( \varepsilon(k) = \varepsilon(-k) \) (system looks the same along +x or –x; the +k state becomes the –k state upon inversion; they must have the same energy).

2. \( \varepsilon(0) \) is a max or min if it is not the crossing point of two bands.

   Proof: \( \varepsilon(k) = \varepsilon(-k) \) is an even function. \( \left. \frac{d\varepsilon}{dk} \right|_0 = 0 \)

3. \( \left. \frac{d\varepsilon}{dk} \right|_{k=\pm \frac{\pi}{a} (BZ \text{ boundaries})} = 0 \) (max or min) if it is not a crossing point of two bands

   Proof: \( \varepsilon\left(\frac{\pi}{a} + \delta\right) = \varepsilon\left(\frac{\pi}{a} + \delta - b\right) = \varepsilon\left(-\frac{\pi}{a} + \delta\right) = \varepsilon\left(\frac{\pi}{a} - \delta\right) \)

   \( \left. \frac{d\varepsilon}{dk} \right|_{\frac{\pi}{a}} = \lim_{\delta \to 0} \frac{\varepsilon\left(\frac{\pi}{a} + \delta\right) - \varepsilon\left(\frac{\pi}{a} - \delta\right)}{2\delta} = 0 \)

3d: Assume the system is invariant under \( O = O_R O_t = \{R \mid t\} \), where \( R \) is a point operation (rotation, reflection, inversion, etc.) and \( t \) is a fractional lattice-vector translation (thus, point operations, screw axes, and glide planes are all included).
The Hamiltonian satisfies \[ OHO^{-1} = H \quad \text{and} \quad HO = OH \]

For example, \( O_R \) could be a rotation operator about \( z \): \( O_R \psi (r) = \psi (R^{-1} r) \)

\[
R = \text{rotation matrix} = \begin{pmatrix}
\cos \theta & -\sin \theta & 0 \\
\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
H \psi_k (r) = \varepsilon_k \psi_k (r) \quad O [H \psi_k (r)] = H [O \psi_k (r)] = \varepsilon_k [O \psi_k (r)]
\]

\( O \psi_k (r) \) is also an eigenfunction with the same eigenvalue.

\[
O \psi_k (r) = O \left[ e^{ik \cdot r} u_k (r) \right] = e^{i k \cdot \left( R^{-1} r - t \right)} u_k \left( R^{-1} r - t \right)
\]

\[
k \cdot (R^{-1} r) = (R \ k) \cdot (RR^{-1} r) = (R \ k) \cdot r
\]

\[
O \psi_k (r) = e^{i (R \ k) \cdot r} e^{-i k \cdot t} u_k \left( R^{-1} r - t \right) = e^{i (R \ k) \cdot r} \times \text{(periodic function)} \quad \text{is a Bloch state with} \ k' = R \ k.
\]

\[
\varepsilon (R \ k) = \varepsilon (k) \quad \varepsilon_n (R \ k) = \varepsilon_n (k) \quad \text{with} \ n \ \text{properly chosen.}
\]
Theorem: $\varepsilon_n(R \mathbf{k}) = \varepsilon_n(\mathbf{k})$ if the system is invariant under $O = O_R O_t = \{R \mid t\}$.

$$\varepsilon_n(R \mathbf{k}) = O_R^{-1} \varepsilon_n(\mathbf{k}) = \varepsilon_n(\mathbf{k})$$

For this discussion, a screw axis is like an ordinary axis; the translational part has no effect; ditto for glide planes.

Theorem: Constant energy surfaces (including the Fermi surface), defined by $\varepsilon_n(\mathbf{k}) = \text{constant}$, have the full point group symmetry of the crystal.

Examples:

If the system has inversion symmetry, $\varepsilon_n(\mathbf{k}) = \varepsilon_n(-\mathbf{k})$.

If the system is symmetric with respect to reflection about the yz plane:

$$\varepsilon_n(k_x, k_y, k_z) = \varepsilon_n(-k_x, k_y, k_z).$$

Etc.

Time reversal:

If we ignore spin, $\psi_{\mathbf{k}}$ and $\psi_{-\mathbf{k}}$ are degenerate, $\varepsilon(\mathbf{k}) = \varepsilon(-\mathbf{k})$; an electron with wave vector $\mathbf{k}$ becomes $-\mathbf{k}$ upon time reversal. Same effect as inversion symmetry.
Spin-orbit interaction: in the rest frame of the electron, the nucleus orbits around it to generate a magnetic field. The electron spin has a magnetic moment. Its energy level splits (Zeeman effect). So, spin degeneracy may be lifted.

If we include $H_{\text{soi}}$ (spin-orbit interaction), $\epsilon_{k\uparrow} = \epsilon_{-k\downarrow}$ ($\epsilon_{k\uparrow} \neq \epsilon_{k\downarrow}$ generally).

Spin degeneracy is lifted for the band (but not at the zone center).

However, if the system also has inversion symmetry, $\epsilon_{k\uparrow} = \epsilon_{-k\uparrow} = \epsilon_{k\downarrow}$, the system becomes spin degenerate.

Summary: lack of inversion symmetry $\Rightarrow$ spin degeneracy is lifted.

This is known as the **Dresselhaus effect** in the bulk; **Rashba effect** at an interface or surface (where inversion symmetry is lifted).

Important for **spintronics**.