Band structures of crystalline Solid.

As atoms come close together to form a solid, their individual eigen-states merged and form "bands". Here a very significant postulation makes a difference, which is identical electron concept.

Now, the general solution of a 3-D crystalline solid can be approximated using the Bloch theorem, which basically invokes the symmetry properties of the "atoms" (or the $U(r)$) to solve the T.I.S.E. The most important consequence is that (under independent electron approx.)

$$\psi(r) = e^{i k \cdot \mathbf{r}} u_k(r),$$

where $u_k(r)$ follows the symmetry of the solid, i.e. $u_k(\mathbf{r} + \mathbf{R}) = u_k(\mathbf{r})$.

$R$ is a lattice constant.
Now just as free-electrons in a large 3-D box, if we use the "periodic boundary conditions," we have

\[ k_x = \frac{2\pi N_x}{L_x} \quad ; \quad N_x = \text{integer} \]

But \[ L_x = N_x \cdot a_x \] with \( N_x \) = number of atoms in \( x \)-direction.
\[ a_x = \text{spacing between atom in the } x \)-direction.

\[ k_x = \frac{2\pi N_x}{N_x \cdot a_x} \]

Just like before, we can think of each \( \mathbf{k} = (k_x, k_y, k_z) \) occupies a volume in the \( k \)-space of \( \frac{(2\pi)^3}{L_x L_y L_z} = \frac{a^3}{V} \)

Now the solution of \( \Psi(k^2) \) is indexed by \( k \) (i.e. there are many solutions to the S.E. for each \( k \))

But! the \( E \)-\( k \) relationships are bands.
Note, since \( \mathbf{k} \) is in \( \mathbb{R}^3 \), satisfying the periodic B.C. and that by symmetry \( U_k(r) = U_k(r+\mathbf{R}) \), we can "restrict" the \( k \)-values in the zone of \( \mathbf{k} \) with \( |k_x| < K_x \), \( |k_y| < K_y \), \( |k_z| < K_z \) with \( \mathbf{K} = (K_x, K_y, K_z) \) the smallest possible vectors to satisfy

\[
\mathbf{K} \cdot \mathbf{R} = 1
\]

Definition: Valence band is the highest energy band fully occupied by \( \varepsilon \) at \( T = 0K \)

Conduction band is the lowest energy band not fully occupied by \( \varepsilon \) at \( T = 0K \)
Now, how about “dynamics”? That is, if we have an electron in a state \( |\Psi(\vec{r}) \rangle \) how will it evolve when an external \( E \)-field is applied? The “semi-classical” approach is used. Namely:

\[
\dot{\vec{r}} = \frac{\partial \omega}{\partial \vec{k}} = \frac{i}{\hbar} \frac{2E}{\vec{k}}
\]

With an external force (e.g. by applying an \( E \)-field)

\[\delta E = F \cdot \dot{\vec{r}} \cdot dt = -gE \vec{v} \cdot dt = -g \vec{E} \frac{1}{\hbar} \frac{2E}{\vec{k}} dt\]

But \( \delta E = (\frac{dE}{dk}) \delta k \)

\[
\Rightarrow \frac{dE}{dk} \delta k = -g \vec{E} \frac{1}{\hbar} \frac{2E}{\vec{k}} dt
\]

Or \( -g \vec{E} = F = \frac{2 \hbar k}{2E} \)

Making an analogy as in classical Mechanics
\[ F = \frac{2P}{\dot{t}} \]

We see that the counterpart is \( \dot{t} \).

We called \( \dot{t} \) the "crystal momentum."

Furthermore, if we want to make the analogy \( P = m \dot{v} \), we see that

\[ \dot{v} = \frac{2E}{2k} \quad \text{and} \quad F = ma = m^* \frac{d\dot{v}}{dt} \]

i.e.

\[ \frac{d\dot{v}}{dt} = \frac{1}{\dot{v}} \left( \frac{1}{\hbar} \frac{dE}{dk} \right) = \frac{1}{\hbar} \frac{2E}{2k} \cdot \frac{2k}{2E} \]

\[ = \frac{12^2 E}{\hbar^2 2k^2} \cdot \frac{2\hbar k}{2E} \]

i.e. the equivalent of mass in classical mechanics is

\[ \frac{\hbar^2}{2E} \]

and is called \( m^* \) (effective mass).
Now, we come to a most amazing consequence of the quantum mechanical nature of solid: A filled band is inert!

\[ J = \sum \frac{-q v_k}{k} = -q \int \frac{v_k}{\hbar k} \, dk \]

\[ = \frac{-8}{8\pi^3} \int \frac{1}{h} \frac{2\xi}{2k} \, dk \]

But by symmetry for each \( \vec{k} \), there is a \( -\vec{k} \) with \( \frac{2\xi}{2k} = -\frac{2\xi}{2k} \)

i.e. \( \int \equiv 0 \)

Insulator: conduction band is empty at \( T = 0K \)

Conductor: conduction band is not empty at \( 0K \)
"Semiconductor": insulator but conduction band has "reasonable" number of $e^-$ at $T = 300\, K$.

Carroll statistics.
Now electron is Fermions and they obey:

$$f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1}$$

For $E \gg E_F$, we can approximate $f(E)$ by

$$e^{-\frac{(E-E_F)}{kT}}$$