Dynamical aspects of electrons in bands

- What else does the band structure tell us about how electrons in solids behave?

- Consider first free electron:

  eigenfunctions: $W(k, x) = \frac{1}{\sqrt{L}} e^{ikx}$

  eigenvalues: $E(k) = \frac{\hbar^2 k^2}{2m}$

- Plane waves are eigenfunctions of momentum:

  $\hat{p}|W_k\rangle = -i\hbar \frac{d}{dx}|W_k\rangle = \hbar k |W_k\rangle$

- Now consider e^- in periodic potential

  * For band $E(k)$, wavefunction $\psi_k(x) = u_k(x) e^{ikx}$

$\langle x|\hat{p}|\psi_k\rangle = -i\hbar \frac{d}{dx}\left[e^{ikx} u_k(x)\right] = \hbar k \psi_k(x) - i\hbar e^{ikx} \frac{d u_k(x)}{dx}$

↳ Bloch function is <u>not</u> an eigenfunction of $\hat{p}$

  * Even though $\hbar k$ is not true momentum of electron, it is still a useful quantity
    - $\hbar k \to$ Crystal (or quasi) momentum

  * Consider the "semiclassical" electron velocity:

    $v(k) \equiv \langle \psi_k | \frac{p}{m} | \psi_k \rangle$

    - we can relate this to $E(k)$ in the following way (see next page)

- Start w/ the relation:

$$\langle \psi_k | \frac{\hat{p}^2}{2m} + \hat{V} | \psi_k \rangle = E_k$$

Express in terms of cell-periodic functions u:

$$\langle \psi_k | \frac{\hat{p}^2}{2m} | \psi_k \rangle = \langle u_k | \frac{(p+\hbar k)^2}{2m} | u_k \rangle$$ ← will show for H.W.

$$\langle \psi_k | \hat{V} | \psi_k \rangle = \langle u_k | \hat{V} | u_k \rangle$$

Now take derivative $\frac{d}{dk}$:

$\hat{H}_k$ is Hamiltonian for cell-periodic part

$$\frac{dE(k)}{dk} = \frac{d}{dk} \langle u_k | \underbrace{\frac{(p+\hbar k)^2}{2m} + V}_{\hat{H}_k} | u_k \rangle$$

$$= \overset{①}{\langle \frac{du_k}{dk} | \hat{H}_k | u_k \rangle} + \overset{②}{\langle u_k | \frac{d}{dk} \frac{(p+\hbar k)^2}{2m} | u_k \rangle}$$

$$+ \overset{③}{\langle u_k | \hat{H}_k | \frac{du_k}{dk} \rangle}$$

① + ③ $= E_k \left(\frac{d}{dk} \langle u_k | u_k \rangle \right) = 0$

② $= \langle u_k | \frac{\hbar}{m} (p + \hbar k) | u_k \rangle$

- Return to full ψ: $$\boxed{\frac{1}{\hbar} \frac{dE(k)}{dk} = \langle \psi_k | \frac{p}{m} | \psi_k \rangle \equiv V(k)}$$

↓

Derivative of band gives semiclassical velocity of electrons

* "Semiclassical": Take some aspects to be quantum, other aspects to be classical

- In our case QM gives us bands, but we consider the electron dynamics as if it were a classical particle (see next page) in classical field.

* What if we consider the interband case, taking:

$$\frac{d}{dk}\left[\frac{1}{2m}(p+\hbar k)^2 + V\right]|u_{nk}\rangle = \frac{d}{dk}\left[E_{nk}\,|u_{nk}\rangle\right]$$

n is band index

$$\Rightarrow \frac{\hbar}{m}(p+\hbar k)|u_{nk}\rangle + H_k\left|\frac{du_{nk}}{dk}\right\rangle = \frac{dE_{nk}}{dk}|u_{nk}\rangle + E_{nk}\left|\frac{du_{nk}}{dk}\right\rangle$$

Now multiply on left by $\langle u_{mk}|$, $m \neq n$:

$$\langle u_{mk}|\frac{\hbar}{m}(p+\hbar k)|u_{nk}\rangle + \langle u_{mk}|H_k\left|\frac{du_{nk}}{dk}\right\rangle = \langle u_{mk}|\frac{dE_{nk}}{dk}|u_{nk}\rangle + E_{nk}\langle u_{mk}\left|\frac{du_{nk}}{dk}\right\rangle$$

$$\Rightarrow \langle u_{mk}|\frac{\hbar}{m}p|u_{nk}\rangle = (E_{nk} - E_{mk})\langle u_{mk}\left|\frac{du_{nk}}{dk}\right\rangle$$

- We can compare this to the expectation value of $[H,x]$ which is a more general way of writing velocity

$\Rightarrow$ why? Heisenberg Eq. of motion: $\frac{\partial x}{\partial t} = \frac{i}{\hbar}[H,x]$ $\leftarrow \vec{r}$ is operator!

$$\langle \psi_{mk}|[H,x]|\psi_{nk}\rangle = (E_{mk} - E_{nk})\langle \psi_{mk}|x|\psi_{nk}\rangle$$

but $[H,x] = \left[\frac{p^2}{2m} + V(\vec{r}), \vec{r}\right] = -i\frac{\hbar}{m}p$

so: $\boxed{\langle u_{mk}|x|u_{nk}\rangle = i\langle u_{mk}|\frac{\partial}{\partial k}u_{nk}\rangle}$

$\uparrow$ interband dipole matrix elements. Important for e.g., optical excitations

* What does crystal momentum $\hbar k$ tell us?

- Consider effect of uniform electric field:

$$H = \frac{p^2}{2m} + V + eFx$$

electric field

(Note, breaks periodicity)

- At some initial time $t_0 = 0$, prepare a Bloch state
- Time evolution will be:

$$\psi(x,t;F) = \exp\left(-\frac{i}{\hbar}Ht\right)\psi(k_0,t)$$

initial Bloch state

- Now translate variable $x \to x+a$:

$$\psi(x+a,t;F) = \exp\left(-\frac{i}{\hbar}Ht\right)\exp\left(-\frac{i}{\hbar}eFa\,t\right)\underbrace{e^{ik_0 a}\,\psi(k_0,x)}_{\text{Bloch's theorem}}$$

nonperiodic part of H

$$= e^{ik(t)a}\,\psi(x,t;F)$$

$$k(t) = -\frac{1}{\hbar}eFt + k_0$$

- Time evolved wavefunction is Bloch-type w/ k changing linearly in time:

$$\boxed{\frac{d[\hbar k(t)]}{dt} = -eF}$$

$\Rightarrow$ Force on electron in periodic potential from electric field is consistent with $p = \hbar k$!!

- Consider a single band. Semiclassical acceleration:

$$\frac{dv(k)}{dt} = \frac{d}{dt}\frac{1}{\hbar}\frac{dE(k)}{dk} = \frac{1}{\hbar}\frac{d^2E(k)}{dk^2}\frac{dk}{dt} = \frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}(-eF)$$

- Newton-like expression $F = m^* a$, $\boxed{\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}}$

Effective mass from band curvature

* Conductivity in bands

- Consider a completely filled band. What is current I?

$$I = \frac{\text{Charge}}{\text{time}} = \underset{\text{for spin, more on this later}}{2} \sum_k -e \frac{v(k)}{L} = -\frac{2e}{L\hbar} \sum_k \frac{dE(k)}{dk} = 0$$

$\sum_k \frac{dE(k)}{dk} = 0$ because $E(k) = E(-k)$ (more on this later)

- Remove one electron at state k_n:

$$I_n = 2 \sum_k -e \frac{v(k)}{L} - (-e) \frac{v(k_n)}{L} = +e \frac{v(k_n)}{L}$$

↳ effective current of "hole" looks like positively charged electron!

- We see that only materials w/ partially filled bands conduct electricity

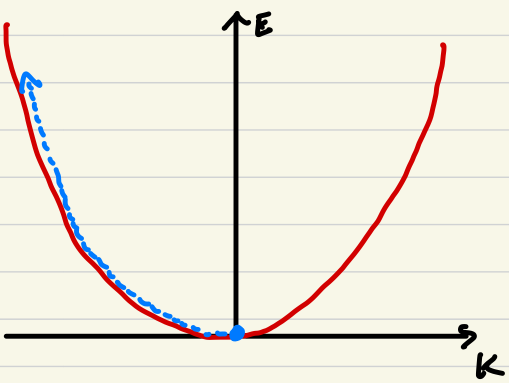
Bloch oscillations

- What will happen if we continue to apply the field?

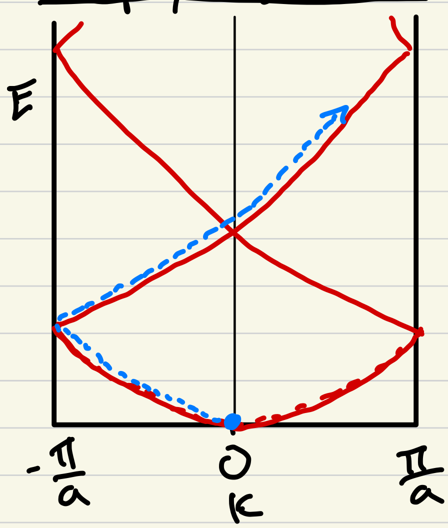
$*$ $k(t) = k_0 - \frac{1}{\hbar} eFt$, $v(t) = \frac{1}{\hbar} \left. \frac{dE(k)}{dk} \right|_{k=k(t)}$

↳ magnitude increases linearly

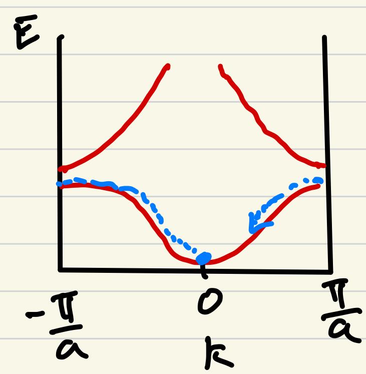
Free electron



Empty lattice



Periodic potential



$*$ Instead of v increasing in time (free electron / empty lattice), electron motion is oscillitory

- Bloch oscillations
- Time T_B, frequency ω_B to complete one oscillation:

$$T_B = \frac{2\pi\hbar}{aeF} , \quad \omega_B = \frac{2\pi}{T_B} = \frac{aeF}{\hbar}$$

- Oscillates in space also. Consider tight-binding band:

$$v(t) = -\frac{2\gamma a}{\hbar} \sin\left[\left(k_0 - \frac{eFt}{\hbar}\right)a\right]$$

so:

$$x(t) = x_0 - \frac{2\gamma}{eF} \cos\left[\left(k_0 - \frac{eFt}{\hbar}\right)a\right]$$

spatial oscillations

* In realistic situations we have scattering
  - No system has perfect periodicity
  - More on scattering later
  - parameterized by a scattering time τ
  - Could only observe Bloch oscillations if:

    $\omega_B \tau \gg 1$ ← Many oscillations before scattering
  - For field of $F = 10^4$ V/cm, $a = 1$ Å $\Rightarrow T_B \sim 10^{-9}$ s
  - Many scattering processes happen on the order of femto or pico seconds
  - In many materials $\omega_B \tau \cancel{\gg} 1$

* <u>NOTE</u>: strictly speaking, F breaks translational symmetry, so the band structure should not be taken too literally
  - Recall, this is a semiclassical approach!

Electrons in 1D periodic potentials: What have we learned?

- Wavefunctions of electrons in periodic potentials can be written as:

$$\boxed{\psi_k(x) = u_k(x)\, e^{ikx} \quad , \qquad k = \frac{2\pi}{Na} n \quad , \quad n \in \mathbb{Z}}$$

- Electrons in a periodic potential form bands
  * Continuous (actually dense but discrete ☺) set of allowed energies for different k separated by gaps
- Can describe Hamiltonians and wavefunction by expanding in an appropriate basis
  * we saw plane waves and atomic orbitals
  * Solving S.E. becomes a matrix diagonalization problem
- Green's Functions can be used to describe properties of system
  * Total and projected DOS
  * Energy eigenvalues (poles of Green's function)
- Combining bands with semiclassical fields gives insight into transport
  * electrons in bands act under fields as if they have crystal momentum and effective mass