Density of States & Greens Functions

- Consider a system described by a Hamiltonian

$$H|\psi_m\rangle = E_m|\psi_m\rangle$$

- Density of states: $D(E) = \sum_m \delta(E - E_m)$

Eigenvalues of H

* Projected density of states for an orbital ϕ_0

$$n_0(E) = \sum_m |\langle\phi_0|\psi_m\rangle|^2 \, \delta(E - E_m)$$

Some basis function

Eigenfunc. of H

- Define the (retarded) Green's Fn:

$$G(E+i\varepsilon) \equiv \frac{1}{(E+i\varepsilon)\mathbb{1} - H}$$

$\to$ $N \times N$ matrix

infinitesimal $\varepsilon > 0$

$N \times N$ identity matrix

* Since H is a matrix, so is G

* Consider the upper left element:

$$G_{00}(E+i\varepsilon) \equiv \langle \phi_0 | \frac{1}{(E+i\varepsilon)-H} | \phi_0 \rangle$$

$$= \langle \phi_0 | \sum_m |\psi_m\rangle\langle\psi_m| \frac{1}{E+i\varepsilon-H} |\phi_0\rangle =$$

$$= \sum_m |\langle \phi_0 | \psi_m\rangle|^2 \frac{1}{E+i\varepsilon-E_m} \left(\frac{E-E_m-i\varepsilon}{E-E_m-i\varepsilon}\right)$$

$$= \sum_m |\langle \phi_0 | \psi_m \rangle|^2 \frac{E-E_m-i\varepsilon}{(E-E_m)^2+\varepsilon^2}$$

$$G_{00}(E+i\varepsilon) = \sum_m |\langle \phi_0 | \psi_m\rangle|^2 \frac{E-E_m-i\varepsilon}{(E-E_m)^2+\varepsilon^2}$$

* Using: $\lim_{\varepsilon \to 0^+} \frac{1}{\pi} \frac{\varepsilon}{(E-E_m)^2+\varepsilon^2} = \delta(E-E_m)$

We can define the PDOS: $\boxed{n_0(E) = -\frac{1}{\pi} \lim_{\varepsilon\to 0^+} \operatorname{Im} G_{00}(E+i\varepsilon)}$

* Summing over diagonal gives Total DOS $\boxed{D(E) = -\frac{1}{\pi} \lim_{\varepsilon\to 0^+} \operatorname{Im} \operatorname{Tr} G(E+i\varepsilon)}$

– Can also get DOS from summing dispersion over k

$$D(E) = \sum_k \delta[E \underbrace{- 2\gamma\cos(ka)}_{\text{1D TB Hamiltonian}}]$$

1D TB Hamiltonian
$E(k) = E_0 - 2\gamma\cos(ka)$ with $E_0 = 0$

* Convert to continuous k:

$$\sum_k \longrightarrow \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} dk \qquad \left(\text{recall } k_n = \frac{2\pi}{Na} n\right)$$

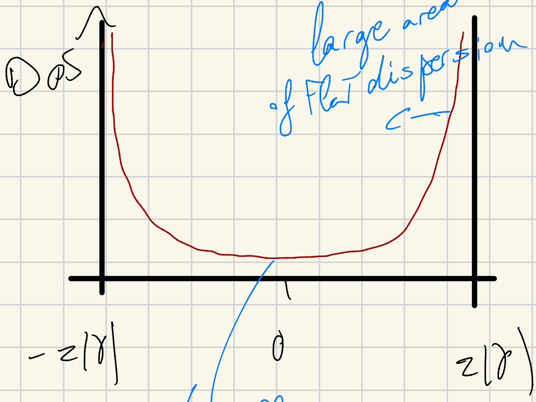
So: $$D(E) = \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} \delta[E - 2\gamma\cos(ka)]$$

Using: $$\delta[f(x)] = \sum_{x_0 \in \text{zeros of } f(x)} \frac{\delta(x - x_0)}{|f'(x_0)|}$$

$$D(E) = \frac{Na}{2\pi} 2 \frac{1}{|2\gamma a \sin(k_0 a)|} \qquad k_0 = \frac{1}{a}\arccos\left(\frac{E}{2\gamma}\right) \text{ So:}$$

$$D(E) = \frac{Na}{\pi}\left[2\gamma a \sin\left[\arccos\left(\frac{E}{2\gamma}\right)\right]\right]^{-1} = \frac{N}{\pi}\frac{1}{\sqrt{4\gamma^2 - E^2}}$$

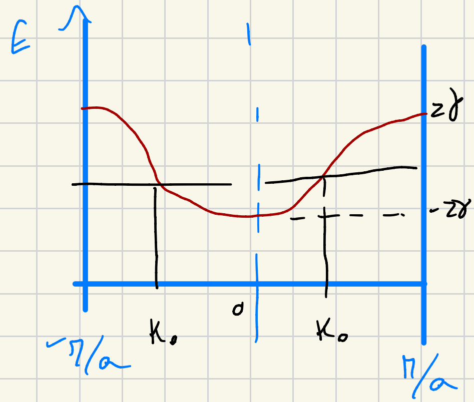
$$= N \cdot n(E) \quad (\text{for } |E| < 2|\gamma|)$$



large areas of flat dispersion (Top & Bottom)

Van Hove singularity

smallest when slope of band is maximum.



Dynamical aspects of e^- in bands

- What else does band structure tell us about how e^- behave?

  - Free e^- : $W(k,x) = \frac{1}{\sqrt{2}} e^{ikx}$; $\epsilon(k) = \frac{\hbar^2 k^2}{2m}$

- Plane waves are eigen fn of momentum:

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

- Now consider e^- in a periodic potential

  → For band $E_n(k)$, WF: $\psi_{n,k}(x) = U_{n,k}(x) e^{ikx}$

$$\hat{p} \, |\psi_{nk}\rangle = \hbar k \, \psi_{n,k}(x) - i\hbar e^{ikx} \frac{d}{dx} U_{n,k}(x)$$

↓

Bloch WF is not an eigenfn of $\hat{p}$

But $\hbar k$, even if it is not the real momentum is still useful. $\hbar k \equiv$ crystal or quasi momentum.

* Consider the "semiclassical" e^- velocity:

$$\vec{V}(k) \equiv \langle \psi_{n,k} | \frac{\hat{P}}{m} | \psi_{n,k} \rangle$$

• We can relate this to $E(k)$:

(x in 1D, $\vec{r}$ in 3D)

$$E_{n,k} = \langle \psi_{nk} | \frac{P^2}{2m} + \hat{V} | \psi_{n,k} \rangle \text{ with } \psi_{nk} = e^{ikx} U_{nk}(x)$$

$$\langle \psi_{nk} | \frac{P^2}{2m} | \psi_{nk} \rangle = \langle U_{nk} | \frac{(P + \hbar k)^2}{2m} | U_{nk} \rangle$$ ← we did this in HW 2

$$\langle \psi_{nk} | V(r) | \psi_{nk} \rangle = \langle U_{nk} | V | U_{nk} \rangle$$

Now take derivative $\frac{d}{dx}$

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

$$\frac{dE_n(k)}{dk} = \frac{d}{dk} \langle U_{nk} | \underbrace{\frac{(P + \hbar k)^2}{2m} + V}_{\hat{H}_k} | U_{nk} \rangle$$

$$= \underset{(1)}{\langle \frac{dU_{nk}}{dk} | H_k | U_{nk} \rangle} + \underset{(2)}{\langle U_{nk} | \frac{d}{dk} \frac{(P + \hbar k)^2}{2m} | U_{nk} \rangle}$$

$$+ \underset{(3)}{\langle U_{nk} | \hat{H}_k | \frac{dU_{nk}}{dk} \rangle}$$

$$(1) + (3) = E_k \left(\frac{d}{dk} \langle U_{nk}, U_{nk} \rangle \right) = 0$$

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

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

derivative of bands gives semiclassical v of e^-

What does semiclassical mean?: Takes some aspects to be quantum and others classical.

- Q : Bands
- C : e^- dynamics considers a classical particle in a classical field.

$\rightarrow$ Note this is all for intraband dynamics (same n in Bra & Ket)

How about interband dynamics?

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

$$\Rightarrow \frac{\hbar^2}{m}(p+\hbar k)|U_{nk}\rangle + H_k\left|\frac{dU_{nk}}{dk}\right\rangle = \frac{dE_{nk}}{dk}|U_{nk}\rangle + E_{nk}\left|\frac{dU_{nk}}{dk}\right\rangle$$

$\Rightarrow$ Now multiply on left by $\langle U_{mk}|$ $m \neq n$

$$\langle u_{m,k} | \frac{\hbar}{m}(p+\hbar k) | u_{nk} \rangle + \langle u_{mk} | H_k | \frac{du_{nk}}{dk} \rangle$$

$$= \langle u_{mk} | \frac{dE_{nk}}{dk} | u_{nk} \rangle + E_{nk} \langle u_{mk} | \frac{du_{nk}}{dk} \rangle$$

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

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

Why? Heisenberg eq. of motion $\frac{d\hat{r}}{dt} = \frac{i}{\hbar}[H, x]$ → operator

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

But $[H, \hat{r}] = \left[\frac{p^2}{2m} + V, \hat{r}\right] = -i\frac{\hbar}{m} p$

So $\langle u_{mk} | r | u_{nk} \rangle = i \langle u_{mk} | \frac{\partial}{\partial k} u_{nk} \rangle$

intraband dipole matrix elements, important for ex for optical excitations

What does $\hbar k$, crystal momentum tells us?

- Consider the effect of a uniform e^- field

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

$\downarrow$ electrix field, Breaks periodicity!

- At $t=0$ 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 $x \to x+a$

$$\psi(x+a,t;F) = \exp\left(-\frac{i}{\hbar}Ht\right)\exp\left(\frac{-i}{\hbar}eFat\right)\underbrace{e^{ik_0a}\psi(k_0,x)}_{\text{Blochs Theorem}}$$

Non periodic part of H

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

$$\downarrow$$

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

- The Time evolved WF is Bloch-Type with k changing linearly with Time

$$\boxed{\frac{d\left[\hbar k(t)\right]}{dt} = -eF}$$ → Force on e^- in periodic potential from e^- field is consistent with $p = \hbar k$!!

- Consider a single band: semiclassical acceleration:

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

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

↙ effective mass from band curvature

* Conductivity in bands:

- Consider a band totally filled. What is the current I?

$$I = \frac{Q}{t} = \underset{\text{spin}}{2}\sum_k -e\frac{v(k)}{L} = \frac{-2e}{L\hbar}\sum_k \frac{dE(k)}{dk} = 0$$

$$\sum_k \frac{dE(k)}{dk} = 0 \quad \text{because } E(k) = E(-k)$$

· Remove an e^- 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 e^-

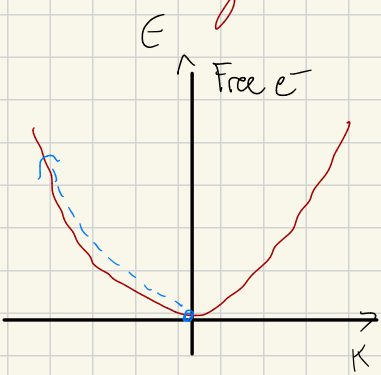
⟶ Only materials with partially filled bands conduct electricity

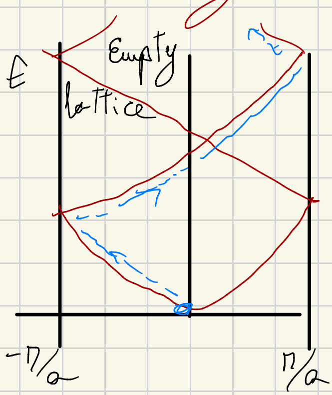
Block oscillations

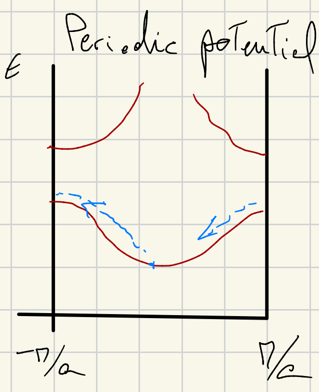
- What will happen if we continue to apply a field?

$\ast$ $k(t) = k_0 - \frac{1}{\hbar} eFt$ $\quad V(t) = \frac{1}{\hbar}\frac{\partial E(k)}{dk}\Big|_{k=k(t)}$

↓ magnitude increases linearly







* Instead of v increasing in time (free e^-, empty lattice) e^- motion will be oscillatory

$\Rightarrow$ Bloch Oscillations

- Time T_B, $\Rightarrow$ frequency to complete 1 oscillation:

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

- Oscillates in space also. Ex consider a TB band

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

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

* But in reality (real materials) we have scattering
  - No system has perfect periodicity
  - more on scattering later
  - Parametrized by scattering time τ
  - Can only observe B.O if $\omega_B \tau \gg 1$ (many oscillations before scattering)

Not true in many materials.