


Density of States & Green's Functions

- Consider a system described by a

Hamiltonian

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

Eigenvalues of H

- Density of States: $\rho(E) = \sum_m \delta(E - E_m)$

* Projected density of states for an orbital ϕ .

$$\rho_\phi(E) = \sum_m |\langle \phi | \psi_m \rangle|^2 \delta(E - E_m)$$

Some basis function

Eigenfunc. of H

- Define the (retarded) Green's Fn:

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

$\rightarrow N \times N$ matrix

infinitesimal $\varepsilon > 0$ $N \times N$ identity matrix

• Since H is a matrix, so is G

* Consider the upper left element:

$$G_{oo}(E+i\epsilon) \equiv \langle \phi_o | \frac{1}{(E+i\epsilon) - H} | \phi_o \rangle$$

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

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

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

$$G_{oo}(E+i\epsilon) = \sum_m |\langle \phi_o | \psi_m \rangle|^2 \frac{E - E_m - i\epsilon}{(E - E_m)^2 + \epsilon^2}$$

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

We can define The PDOS: $\rho_o(E) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} G_{oo}(E+i\epsilon)$

* Summing over diagonal

gives Total DOS

$$\rho(E) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} \text{Tr} G(E+i\epsilon)$$

- Can also get DOS from summing dispersion over k

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

1D TB Hamiltonian

$$E(k) = E_0 - 2\gamma \cos(ka) \text{ with } E_0 = 0$$

Convert To continuous k :

$$\sum_k \rightarrow \frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} dk \quad \left(\text{recall } k = \frac{2\pi}{Na} n \right)$$

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

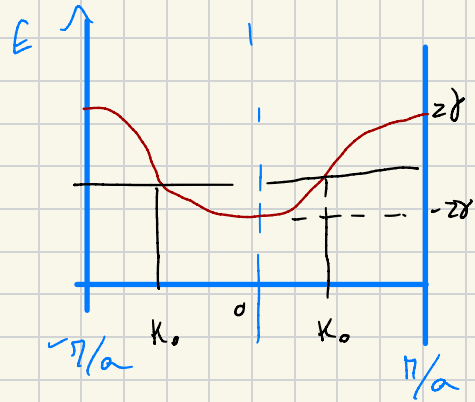
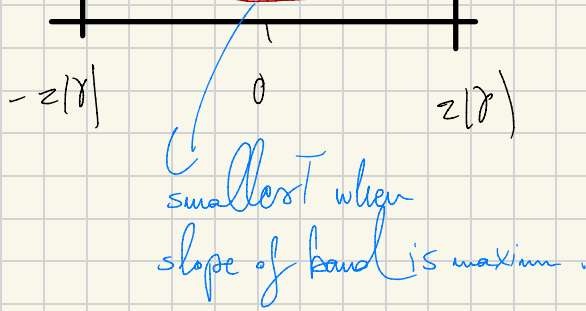
Using:

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

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

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

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



Dynamical aspects of e^- in bands

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

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

- 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: $\psi_{n,k}(x) = U_{n,k}(x) e^{ikx}$

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

↓
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 $E(k)$:

$$E_{n,k} = \langle \psi_{n,k} | \frac{p^2}{2m} + \hat{V} | \psi_{n,k} \rangle \text{ with } \psi_{n,k} = e^{ikx} U_{n,k}(x) \quad \left(\begin{array}{l} x \text{ in 1D} \\ \vec{r} \text{ in 3D} \end{array} \right)$$

$$\langle \psi_{n,k} | \frac{p^2}{2m} | \psi_{n,k} \rangle = \langle U_{n,k} | \frac{(p + \hbar k)^2}{2m} | U_{n,k} \rangle \quad \leftarrow \text{we did this in HW 2}$$

$$\langle \psi_{n,k} | V(r) | \psi_{n,k} \rangle = \langle U_{n,k} | V | U_{n,k} \rangle$$

Now Take derivative $\frac{d}{dk}$ $\nearrow \hat{H}_k$ is hamiltonian for cell-periodic part

$$\frac{dE_n(k)}{dk} = \frac{d}{dk} \langle U_{n,k} | \frac{(p + \hbar k)^2}{2m} + V | U_{n,k} \rangle$$

$$= \underbrace{\langle \frac{dU_{n,k}}{dk} | \hat{H}_k | U_{n,k} \rangle}_{(1)} + \underbrace{\langle U_{n,k} | \frac{d}{dk} \frac{(p + \hbar k)^2}{2m} | U_{n,k} \rangle}_{(2)}$$

$$+ \langle U_{n,k} | \hat{H}_k | \frac{dU_{n,k}}{dk} \rangle \quad (1) + (3) = E_n \left(\frac{d}{dk} \langle U_{n,k}, U_{n,k} \rangle \right) = 0$$

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

Return To hell ψ :

$$\frac{1}{\hbar} \frac{dE(k)}{dk} = \langle \psi_{nk} | \frac{p}{m} | \psi_{nk} \rangle \equiv V(k)$$

↓
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.

→ Note This is all for intraband dynamics (same n in Bra & Ket)

How about interband dynamics?

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

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

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

$$\begin{aligned}
& \langle U_{m,k} | \frac{\hbar}{m} (p + \hbar k) | U_{n,k} \rangle + \langle U_{m,k} | H_k \rangle \frac{dU_{n,k}}{dk} \\
&= \langle U_{m,k} | \frac{dE_{n,k}}{dk} | U_{n,k} \rangle + E_{n,k} \langle U_{m,k} | \frac{dU_{n,k}}{dk} \rangle \\
&\Rightarrow \langle U_{m,k} | \frac{\hbar}{m} p | U_{n,k} \rangle = (E_{n,k} - E_{m,k}) \langle U_{m,k} | \frac{dU_{n,k}}{dk} \rangle
\end{aligned}$$

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

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

$$\langle \psi_{m,k} | [H, \hat{r}] | \psi_{n,k} \rangle = (E_{m,k} - E_{n,k}) \langle \psi_{m,k} | \hat{r} | \psi_{n,k} \rangle$$

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

$$\text{So } \langle U_{m,k} | \hat{r} | U_{n,k} \rangle = i \langle U_{m,k} | \frac{\partial}{\partial k} U_{n,k} \rangle$$

↑
intra-band 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

$$H = \frac{p^2}{2m} + U + e F x$$

↓ electric field, Breaks periodicity!

- At $t=0$ prepare a Bloch state

Time evolution will be:

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

→ initial Bloch state

- Now Translate variable $x \rightarrow x+a$

$$\Psi(x+a, t; F) = \exp\left(-\frac{i}{\hbar} H t\right) \exp\left(-\frac{i}{\hbar} e F a t\right) e^{ik_0 a} \Psi(k_0, x)$$

Non periodic part of H

Bloch's Theorem

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

$$\downarrow k(t) = -\frac{1}{\hbar} e F t + k_0$$

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

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

Force on e^- in periodic potential from e^- field is consistent with $p = \hbar k$!!

- Consider a single band: semiclassical acceleration:

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

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

effective mass from band curvature

* Conductivity in bands:

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

$$I = \frac{Q}{t} = \sum_{\substack{\text{spin} \\ k}} -e \frac{V(k)}{L} = \frac{-ze}{L\hbar} \sum_k \frac{dE(k)}{dk} = 0$$

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

• 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^-

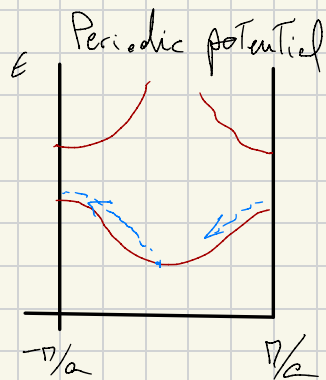
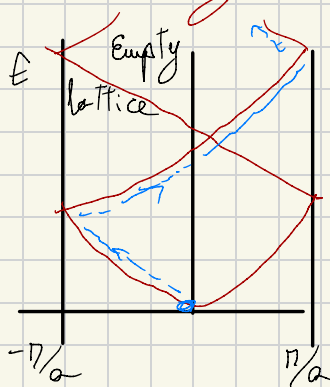
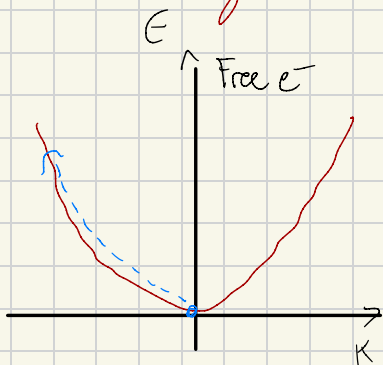
⇒ Only materials with partially filled bands conduct electricity

Bloch oscillations

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

$$* k(t) = k_0 - \frac{1}{\hbar} e F t \quad V(t) = \frac{1}{\hbar} \frac{\partial E(k)}{\partial k} \bigg|_{k=k(t)}$$

↓ 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:

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

- Oscillates in space also. Ex consider a TB band

$$V(t) = -\frac{eFa}{\hbar} \sin\left[\left(k_0 - \frac{eFt}{\hbar}\right)a\right]$$

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

* 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.