LECTURE #3

9/15 ①

To describe the interaction between an electromagnetic field & the electrons and ions in a solid, we need to replace $\vec{P}_{e \text{ or ion}}$ by

$$\vec{P}_K + \frac{Z_K e}{c} \vec{A}$$

USE WEYL'S GAUGE: $\varphi \equiv 0$

K index for both electrons & ions

THIS INTRODUCES a perturbation of the form:

$$\Rightarrow \sum_K \frac{Z_K^2 e^2}{2 M_K c^2} |A|^2 + \frac{1}{2} \frac{Z_K e}{M_K c} \left[\vec{P}_K \cdot \vec{A} + \vec{A} \cdot \vec{P}_K \right.$$

Here $\Rightarrow \vec{A} = \vec{A}_0 e^{-i\omega t} \sum_K e^{i \vec{k} \cdot \vec{r}_K} + c.c.$

(WE IGNORE RELATIVISTIC EFFECTS: SPIN, SO...)

- WE ARE INTERESTED IN LINEAR RESPONSE $\Rightarrow$ IGNORE $|A|^2$ TERM

- DIPOLE APPROXIMATION:

$$\vec{A} \approx \vec{A}_0 e^{-i\omega t} + \vec{A}_0^* e^{i\omega t}$$

THE DIPOLE APPROXIMATION IS ACTUALLY VERY GOOD SINCE

$$\Rightarrow \quad k_{LIGHT} \ll k_{BZ} \sim \frac{\pi}{a} \qquad (\lambda_{LIGHT} \gg a)$$

(SAME AS $\lambda_{LIGHT} \gg a_{BOHR}$)

IN THIS APPROXIMATION:

$$\hat{V}_{PERT} = \frac{1}{2} \sum_{\substack{\text{IONS}\\ \text{ELECTRONS}}} \frac{Z_k e}{M_k c} \vec{P}_k \cdot [\vec{A}_0 e^{-i\omega t} + c.c]$$

$\times e^{\gamma t}$

WE WANT TO MAKE A FEW CHANGES IN $\hat{V}$ BEFORE CONTINUING:

1. $$\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} \Rightarrow \vec{E}_0 = \frac{i\omega \vec{A}_0}{c}$$

2. $$\frac{\vec{P}_k}{M_k} = \dot{\vec{r}}_i \equiv \frac{i}{\hbar}[\hat{H}_0, \vec{r}]$$

VELOCITY OPERATOR

$$\hat{H} = \hat{H}_0 + \hat{V}_{PERT}$$

$$\Rightarrow \sum_k \frac{Z_k e}{c} \frac{\hat{P}_k}{M_k} \equiv \frac{i}{\hbar c}\left[\hat{H}_0, \sum_k Z_k e \vec{r}_k\right]$$

$$\sum_k Z_k e_k \vec{r}_k \equiv \text{TOTAL DIPOLE MOMENT OPERATOR}$$

USING THAT

$$\vec{\mathbb{P}} \text{ (POLARIZATION)} \equiv \frac{\text{TOTAL DIPOLE MOMENT}}{\text{VOLUME}}$$

WE GET

$$\Rightarrow \sum_{K} Z_K e \vec{r}_K = V_{\text{OLUME}} \vec{P}$$

THUS

$$\Rightarrow \hat{V}_{\text{PERT}} = \frac{V_{\text{OLUME}}}{2\hbar\omega} [\hat{H}_0, \vec{\mathbb{P}}] [\vec{E}_0 e^{-i\omega t} + \text{c.c.}] \times e^{\gamma t}$$

OUR GOAL NOW IS TO FIND AN EXPRESSION FOR THE SUSCEPTIBILITY DEFINED AS

$$\langle \vec{P}(\omega) \rangle = \chi(\omega) \vec{E}_0$$

EXPECTATION VALUE OF OPERATOR $\vec{P}$

PROCEDURE

ASSUME THAT $\Psi_{\text{SOLID}} \equiv \Psi_{\text{GROUND STATE}}$

FOR $t \to -\infty$

USING TIME-DEPENDENT PERTURBATION THEORY, WE GET

- $$\Psi_G = \Psi_G^{(0)} + \sum_{m \neq G} a_{mG} \, \Psi_m^{(0)}$$

PERTURBED GROUND STATE

GROUND STATE FOR $A = 0$

mth STATE FOR $A = 0$

WHERE

- $$i\hbar \frac{d a_{mG}}{dt} = \langle \Psi_m^{(0)} | \hat{V}_{PERT} | \Psi_G^{(0)} \rangle$$

- CALCULATE $\langle \Psi_G | \vec{P} | \Psi_G \rangle \equiv$

$$\equiv \Big\langle \Psi_G^{(0)} + \sum_m a_{mG} \Psi_m^{(0)} \Big| \vec{P} \Big| \Psi_G^{(0)} + \sum_m a_{mG} \Psi_m^{(0)} \Big\rangle$$

$$\approx \cancel{\langle \Psi_G^{(0)} | \vec{P} | \Psi_G^{(0)} \rangle} + \sum_m \Big\{ a_{mG}^* \langle \Psi_m^{(0)} | \vec{P} | \Psi_G^{(0)} \rangle$$

$$+ \; a_{mG} \langle \Psi_G^{(0)} | \vec{P} | \Psi_m^{(0)} \rangle \Big\} + \cancel{O(a_{mG}^2)}$$

- $$\approx \sum a_{mG}^* \, e^{+i\omega_m t} P_{mG} + a_{mG} \, e^{-i\omega_m t} P_{Gm}$$

NEXT, CALCULATE a_{mG}

$$i\hbar \frac{d a_{mG}}{dt} = \left\langle \Psi_m^{(0)} \middle| \hat{V}_{PERT} \middle| \Psi_G^{(0)} \right\rangle$$

$$\hat{V}_{PERT} = \frac{V_{OLUME}}{2\hbar\omega} \left[\hat{H}_0, \vec{P}\right] \cdot \left[\vec{E}_0 e^{-i(\omega + i\gamma)t} + \vec{E}_0^* e^{i(\omega - i\gamma)t} \right]$$

NOW,

$$\left[\hat{H}_0, \vec{P}\right] = -i\hbar \dot{\vec{P}}$$

THEREFORE

$$\left\langle \Psi_m^{(0)} \middle| \left[\hat{H}_0, \vec{P}\right] \middle| \Psi_G^{(0)} \right\rangle \equiv$$

$$\equiv -i\hbar \left\langle \Psi_m^{(0)} \middle| \dot{\vec{P}} \middle| \Psi_G^{(0)} \right\rangle \equiv$$

$$= \hbar\omega_m \vec{P}_{m,G} e^{i\omega_m t}$$

THEREFORE,

$$\langle \psi_m^{(0)} | \hat{V}_{PERT} | V_G^{(0)} \rangle = \frac{\text{VOLUME}}{2\hbar\omega}\left(\hbar\omega_m\right)$$

$$\times \vec{P}_{mG} \cdot \left[\vec{E}_0 \, e^{-i(\omega - \omega_m + i\gamma)t} + \vec{E}_0^{*} \, e^{i(\omega + \omega_m + i\gamma)t} \right]$$

$$\equiv i\hbar \frac{d a_{mG}}{dt}$$

$$\Rightarrow a_{mG} \equiv \frac{\text{VOLUME}}{2\hbar\omega} \, \omega_m \, \vec{P}_{mG} \cdot e^{i\omega_m t}$$

$$\left[\frac{\vec{E}_0 \, e^{-i(\omega - \cancel{\omega_m} - i\gamma)t}}{\omega - \omega_m - i\gamma} - \frac{\vec{E}_0^{*} \, e^{i(\omega + \cancel{\omega_m} + i\gamma)t}}{\omega + \omega_m + i\gamma} \right]$$

FINALLY,

$$\langle \Psi_G | \vec{P} | \Psi_G \rangle =$$

PERTURBED

$$= \sum_m a^*_{mG}\, e^{i\omega_m t}\, \vec{P}_{mG} + a_{mG}\, e^{-i\omega_m t}\, \vec{P}_{Gm}$$

$$= \frac{\text{VOLUME}}{2\hbar\omega}\,\omega_m \left\{ \vec{P}_{mG}\, \vec{P}^*_{mG} \cdot \left[\frac{\vec{E}_0^*\, e^{i(\omega - i\gamma)t}}{\omega - \omega_m - i\gamma} - \frac{\vec{E}_0\, e^{-i(\omega + i\gamma)t}}{\omega + \omega_m + i\gamma} \right] + \vec{P}_{Gm}\, \vec{P}_{mG} \cdot \left[\frac{\vec{E}_0\, e^{-i(\omega + i\gamma)t}}{\omega - \omega_m + i\gamma} - \frac{\vec{E}_0^*\, e^{i(\omega - i\gamma)t}}{\omega + \omega_m - i\gamma} \right] \right\}$$

NOTE: $\vec{P}_{Gm} \equiv \vec{P}^*_{mG}$

ASSUME ISOTROPIC SOLID

$\Rightarrow \langle |\vec{P}| \rangle$ IS ALONG $\vec{E}_0$

TAKE "x" AS THE DIRECTION OF ELECTRIC FIELD. THEN,

$$\langle |P_x| \rangle = \frac{\text{Volume}}{2\hbar\omega} \sum_m \omega_m |P_{mG}|_x^2$$

$$\times \left\{ \frac{e^{\gamma t}}{\omega-\omega_m+i\gamma} \underbrace{\left[E_0 e^{-i\omega t} + E_0^* e^{i\omega t} \right]}_{\text{FIELD}} \right.$$

$$\left. + \frac{e^{\gamma t}}{\omega+\omega_m+i\gamma} \underbrace{\left[E_0 e^{-i\omega t} + E_0^* e^{i\omega t} \right]}_{\text{FIELD}} \right\}$$

THUS,

$$\chi(\omega) \equiv \frac{\text{Volume}}{2K\omega} \sum_m \omega_m |P_{mG}|^2 \left\{ \frac{1}{\omega-\omega_m-i\gamma} - \right.$$

TRANSVERSE SUSCEPTIBILITY

$$\left. - \frac{1}{\omega+\omega_m+i\gamma} \right\}$$

$$\chi_1(\omega) = \frac{V_{OLUME}}{\hbar\omega} \sum_m \frac{\omega_m^2 \, |\mathbb{P}_{mG}|^2}{\omega_m^2 - \omega^2}$$

PRINCIPAL VALUE

$$\chi_2(\omega) = \frac{\pi V_{OLUME}}{2\hbar\omega} \sum_m \omega_m |\mathbb{P}_{mG}|^2 \times \left[\delta(\omega - \omega_m) + \delta(\omega + \omega_m)\right]$$

FERMI'S GOLDEN RULE

$$\boxed{\lim_{\gamma \to 0^+} \frac{1}{x - i\gamma} \equiv \mathcal{P}\frac{1}{x} + i\pi\delta(x)}$$

$$\vec{\mathbb{P}}_{mG} = \frac{1}{V_{OLUME}} \left\langle \Psi_m \middle| \sum_k Z_k e \vec{r}_k \middle| \Psi_{GS} \right\rangle$$

OK FOR MOLECULES, BUT IT LEADS TO PROBLEMS IN SOLIDS

IT'S BETTER TO GO BACK TO MOMENTUM REPRESENTATION:

$$\vec{P}_k = \frac{i M_k}{\hbar} \left[\hat{H}_0, \vec{r}_k\right]$$

DON'T CONFUSE MOMENTUM WITH DIPOLE

THUS

$$\langle \Psi_m | \vec{P}_k | \Psi_{GS} \rangle = \frac{-i M_k \omega_m}{} \langle \Psi_m | \vec{r}_k | \Psi_{GS} \rangle$$

AND

$$\langle \Psi_m | \underbrace{\sum_k Z_k e \vec{r}_k}_{\vec{P}V} | \Psi_{GS} \rangle \equiv \frac{i e}{\omega_m} \langle \Psi_m | \sum_k \frac{Z_k \vec{P}_k}{M_k} | \Psi_{GS} \rangle$$

WITH THIS,

$$\chi_1(\omega) \equiv \frac{1}{V_{OLUME}} \left(\frac{1}{\hbar \omega} \right) \sum_{mk} \frac{\left| \langle \Psi_m | \sum \frac{Z_k e}{M_k} P_k | \Psi_{GS} \rangle \right|^2}{\omega_m^2 - \omega^2}$$

$$\chi_2(\omega) \equiv \frac{\pi}{2 \hbar \omega^2 V_{OLUME}} \sum \left| \langle \Psi_m | \sum \frac{Z_k e P_k}{M_k} | \Psi_{GS} \rangle \right|^2 \times \left[\delta(\omega - \omega_m) + \delta(\omega + \omega_m) \right]$$

WHAT ARE THE INTERMEDIATE STATES ?

BORN-OPPENHEIMER APPROX.

$$\langle \Psi_m | \equiv \langle \Psi_{ELECTRONS} \times \Psi_{IONS} |$$

$$\sum_k e Z_k r_k \equiv \sum_{IONS} + \sum_{ELECTRONS}$$

$$\chi \equiv \chi_{IONS} + \chi_{ELECTRONS}$$