

Extending The Oscillator Model To Solid State - First The Quantum Approach

Oscillator Strength

→ Schrodinger

$$i\hbar \frac{d\psi}{dt} = H \psi = (H_0 + H') \psi \quad (1)$$

Without a field

$$\begin{cases} \psi_1 = \tilde{\psi}_1 e^{-iE_1/\hbar t} & H_0 \tilde{\psi}_1 = E_1 \tilde{\psi}_1 \\ \psi_2 = \tilde{\psi}_2 e^{-iE_2/\hbar t} & H_0 \tilde{\psi}_2 = E_2 \tilde{\psi}_2 \end{cases}$$

In general $\psi = a(t) \tilde{\psi}_1 + b(t) \tilde{\psi}_2$
 $\tilde{\psi}_1$ and $\tilde{\psi}_2 \rightarrow$ orthonormal

Dipole moment depends upon the superposition

$\psi \psi^* \rightarrow$ probability

$$\int \psi \psi^*(q, \vec{r}) dV \rightarrow \text{expectation of } \vec{p}$$

$$= a(t) b^*(t) \int \tilde{\psi}_1(q, \vec{r}) \tilde{\psi}_2 dV + c.c.$$

$$+ a a^* \int |\tilde{\psi}_1|^2 q \vec{r} dV + b b^* \int |\tilde{\psi}_2|^2 q \vec{r} dV$$

$\tilde{\psi}_1$ or $\tilde{\psi}_2 \rightarrow$ in many cases symmetric or antisymmetric \rightarrow then last two terms are 0

$$\int \tilde{\psi}_1(q, \vec{r}) \tilde{\psi}_2^* dV = \vec{p}_{12} = \text{dipole matrix element}$$

$$= \vec{p}_{12} e^{i(E_2 - E_1)/\hbar t} \quad (2)$$

Thus the superposition is important for the development of the dipole

Schroedinger.

$$i\hbar \frac{\partial \psi}{\partial t} = H_0 \psi + H' \psi \quad H' = -\vec{E} \cdot \vec{p}$$

$$\vec{E} = \vec{E} e^{i\omega t} + c.c.$$

Multiply by ψ_1^* and ψ_2^* to get two equations

$$\textcircled{3} \quad i\hbar \frac{da}{dt} = E_1 a - \int \psi_1^* (\vec{p} \cdot \vec{E}) \psi_2 dV e^{i\omega t} b$$

$$\textcircled{4} \quad i\hbar \frac{db}{dt} = E_2 b - \int \psi_2^* (\vec{p} \cdot \vec{E}) \psi_1 dV e^{-i\omega t} a$$

multiply $\textcircled{3}$ by b^* and $\textcircled{4}^*$ by a and subtract

$$\textcircled{5} \quad - \quad i\hbar \frac{d(ab^*)}{dt} = (E_1 - E_2) ab^* - \int \psi_2^* (\vec{p} \cdot \vec{E}) \psi_1 dV (bb^* - aa^*) e^{+i\omega t}$$

If $(bb^* - aa^*)$ is a constant (constant population difference)

$$ab^* = \frac{\int \psi_2^* (\vec{p} \cdot \vec{E}) \psi_1 dV (bb^* - aa^*)}{\hbar (\omega - \frac{E_2 - E_1}{\hbar})} e^{i\omega t}$$

$$\text{and } \vec{p} = \int \psi_2^* \vec{p} \psi_1 dV ab^*$$

Thus

$$\bar{P} = \frac{\tilde{P}_{12}^* \tilde{P}_{12} + E}{\hbar (\omega - (E_2 - E_1)/\hbar)} e^{i\omega t}$$

Compare with our classical result

$$\begin{aligned} \bar{P} &= \frac{q^2 \tilde{E} e^{i\omega t}}{m (\omega_0^2 - \omega^2 + i\gamma\omega)} \\ &\approx \frac{q^2 \tilde{E} e^{i\omega t}}{m 2\omega_0 (\omega_0 - \omega + 2i\gamma)} \end{aligned}$$

- Upper level population $bb^* = 0$
- Lower level probability, $aa^* = 1$
- Introduce an oscillator strength f

$$f = \frac{(\tilde{P}_{12}^* \tilde{P}_{12} 2\omega_0 m)}{\hbar q^2}$$

into the classical result will give the quantum result if $\omega_0 = (E_2 - E_1)/\hbar$

- Damping missing in the quantum results can be introduced into Eq. (5) by letting $(E_1 - E_2) \rightarrow E_1 - E_2 + 2i\gamma$

(4)

If bb^* and aa^* vary in time

Multiply (3) by a^* and subtract (3)* $\times a$.

This gives

$$i\hbar \frac{\partial aa^*}{\partial t} = - \vec{p}_{12} \cdot \vec{E} e^{i\omega t} (a^* b) + (\vec{p}_{12} \cdot \vec{E})^* e^{-i\omega t} (a b^*)$$

and similarly for (4) $\times b^* - (4)^* \times b$

$$i\hbar \frac{\partial bb^*}{\partial t} = + \vec{p}_{12} \cdot \vec{E} e^{i\omega t} (a^* b) - (\vec{p}_{12} \cdot \vec{E})^* e^{-i\omega t} a b^*$$

These are just energy conservation conditions

$$\begin{aligned} \frac{d(aa^*)}{dt} &= \frac{1}{i\hbar} (- \vec{p} \cdot \vec{E} e^{+i\omega t} + \text{c.c.}) \\ &= \frac{1}{\hbar \omega} (+ i\omega \vec{p} \cdot \vec{E} e^{+i\omega t} - i\omega \vec{p} \cdot \vec{E}^* e^{-i\omega t}) \\ &= - \frac{\text{Re} (\vec{E} \cdot \frac{d\vec{p}}{dt})}{\hbar \omega} \quad \text{time avg} \end{aligned}$$

$$\frac{d\text{Number}}{dt} = - \left(\frac{\text{Power into system}}{\hbar \omega} \right)$$

$$= - \text{Photon number per unit time}$$

Conclusion: There is an intimate relationship of the classical Lorentz model to the quantum picture.

To extend these results to solids

Not $\frac{1}{\omega - (E_2 - E_1)/\hbar}$

does not obey Kramers Kronig

$\frac{1}{\omega - (E_2 - E_1)/\hbar + i2\delta}$

is fine near the resonance but does not converge quickly enough as $\omega \rightarrow \infty \rightarrow$ need the full resonance if Kramers Kronig is to be used.

Note

$$\frac{1}{\Delta\omega + i2\delta} = \frac{1}{(\Delta\omega)^2 + (2\delta)^2} [\Delta\omega - i2\delta]$$

Imaginary part $\rightarrow -\pi i \delta(\Delta\omega)$ as $\delta \rightarrow 0$

$$\begin{aligned} \text{Now } E_2 &\rightarrow E_2(k_2); \psi_2(E_2) = e^{i\mathbf{k}_2 \cdot \mathbf{r} - iE_2(k_2)/\hbar} \\ E_1 &\rightarrow E_1(k_1); \psi_1(E_1) = e^{i\mathbf{k}_1 \cdot \mathbf{r} - iE_1(k_1)/\hbar} \end{aligned}$$

To find total polarization sum over

k_2 and k_1 values. To enumerate

these we assume periodic wave functions

$$k_{1x} L_x = n(2\pi) \quad \text{and similarly}$$

$$k_{1y} L_y = m(2\pi) \quad \text{for } k_2$$

$$k_{1z} L_z = p(2\pi)$$

$$L_x = N a_x; \quad a_x = \text{cell length in } x \text{ direction}$$

$N = \text{no of cells}$

$$\therefore k_{1x} = m \left(\frac{2\pi}{N a_x} \right) \quad m = -\frac{N}{2} \rightarrow \frac{N}{2}$$

$$\text{For differential limit volume/unit k-space} = \frac{(2\pi)^3}{L_x L_y L_z}$$