April 3, 2007

LECTURE #20

Quantum Generalization of
The Lorentz Model
Rigorous deduction of the oscillator strength

The Lorentz and Drude Models and Their extension to Quantum Mechanical Two Level Systems.

Basic model - Lorentz

charge q, field $\bar{E}$, mass m constrainted by a spring with viscous forces included

$$\underbrace{m\frac{d^2\bar{x}}{dt^2}}_{\text{inertial}} + \underbrace{\Gamma m\frac{d\bar{x}}{dt}}_{\text{viscous}} + \underbrace{m\omega_0^2\bar{x}}_{\text{potential energy}} = q\bar{E} \qquad (1)$$

$\omega_0 = \sqrt{k/m}$; k = spring constant.

Extension to 2 level quantum system

$H|\psi_2\rangle = E_2|\psi_2\rangle$; E_2 ———— 2 $|\psi_2\rangle$

$\omega_0 = (E_2 - E_1)/\hbar$

$H|\psi_1\rangle = E_1|\psi_1\rangle$; E_1 ———— 1 $|\psi_1\rangle$

- Dipole moment / Vol $= Nqx$; $N = N_0/m^3$
- For quantum system $N \rightarrow (N_2(t) - N_1(t))$

  $N_2(t)$ = upper level population density

  $N_1(t)$ = lower " "
- Equation for $N_2(t) - N_1(t)$

$$\frac{\partial(N_2(t) - N_1(t))}{\partial t} = +2\bar{E}\cdot\frac{\partial\bar{P}}{\partial t} - \frac{1}{T_1}\underbrace{\partial[N_2(t) - N_1(t)] - (N_{20} - N_{10})]}_{\text{simple relaxation to an equilibrium population difference with charateristic time } T_1 \text{ (Markov Approx)}}$$

rate of energy flow into the system

when system leaves ψ_1 it necessarily goes into ψ_2 (closed)

— <u>Oscillator</u> strength - rigorous derivation

quantum system does not necessarily correspond to 1 full electron making the transition. Introduce the oscillator strength f by writing (1) as

$$\frac{d^2\bar{p}}{dt^2} + \Gamma \frac{d\bar{p}}{dt} + \omega_0^2 \bar{p} = f \frac{q^2}{m} (N_1 - N_2) \bar{E} \qquad (1)$$

Form of f

1) Involves dipole perturbation

$$\mu_{21} \cdot E \qquad \mu_{21} = \underbrace{\int \psi_2^* e \bar{r} \psi_1 \, dV}_{\text{Dipole coupling between states 2 and 1}}$$

This enters through the Schroedinger Equation $\quad H = H_0 - \bar{p} \cdot \bar{E}$

$$H |\psi\rangle = i\hbar \frac{\partial |\psi\rangle}{\partial t}$$

Let $|\psi\rangle = |\psi'\rangle e^{-i H_0/\hbar \, t}$ so

Now consider the expectation of the dipole <u>moment</u> Letting $|\psi\rangle$ be a linear superposition of $|\psi_1'\rangle$ and $|\psi_2'\rangle$,

$$\boxed{|\psi\rangle = A(t)|\psi_1'\rangle e^{-iE_1/\hbar \, t} + B(t)|\psi_2'\rangle e^{-iE_2/\hbar \, t}} \qquad (2)$$

where $H_0|\psi_1'\rangle = E_1|\psi_1'\rangle$ and $H_0|\psi_2'\rangle = E_2|\psi_2'\rangle$

<u>Consider</u> $\langle\psi|p|\psi\rangle$: Generally $\langle 1|p|1\rangle$ and $\langle 2|p|2\rangle$ are taken as zero (why?).

So

$$\langle\psi|p|\psi\rangle = A^*(t) B(t) \langle\psi_1'|p|\psi_2'\rangle e^{i(E_1 - E_2)/\hbar \, t} + c.c. \qquad (3)$$

$\langle\psi_1'|$ and $\langle\psi_2'|$ are "stationary" eigenstates and thus are independent of time $\langle\psi_1'|\psi_1'\rangle = \langle\psi_2'|\psi_2'\rangle = 1$

Take the time derivative of $\langle\psi_1|p|\psi_2\rangle$ (3)

(4) $$\frac{\partial}{\partial t}\langle\psi|p|\psi\rangle = \left(\frac{\partial A^*(t)}{\partial t}B(t) + A^*(t)\frac{\partial B(t)}{\partial t}\right)e^{i(E_1-E_2)t/\hbar}\langle\psi_1'|\bar{p}|\psi_2'\rangle$$

$$+\boxed{e^{\frac{i}{\hbar}(E_1-E_2)t}A^*(t)B(t)\frac{i(E_1-E_2)}{\hbar}\langle\psi_1'|p|\psi_2'\rangle \quad + \quad \text{complex conjugate}}$$

This is just $\frac{i}{\hbar}(E_2-E_1)\times\langle\psi|p|\psi\rangle$ from the previous page

<u>Now apply perturbation:</u>

1) Start out in lower state $|\psi_1'\rangle$ and assume the change in this is small. $|\psi_2'\rangle$ is initially unoccupied. Thus at $t=0$

$$\langle\psi_1'|\psi_1'\rangle = 1 \qquad \langle\psi_2'|\psi_2'\rangle = 0$$

(we must always have $\langle\psi_1'|\psi_1'\rangle + \langle\psi_2'|\psi_2'\rangle = 1$

As an example a 1% change in $|\psi_1'\rangle$ is small but the change in $|\psi_2'\rangle$ is significant since it was unoccupied initially)

2) $|\psi\rangle$ satisfies the Schroedinger Equation $H|\psi\rangle = i\hbar\frac{\partial|\psi\rangle}{\partial t}$ with $H = H_0 + \bar{p}\cdot E$.

3) Taking $\langle\psi_1'|$ and $\langle\psi_2'|$, respectively

$$\langle\psi_1'|H_0 - \bar{p}\cdot\bar{E}|\psi\rangle = \left(i\hbar\frac{\partial A_1}{\partial t} + E_1 A\right)e^{-iE_1/\hbar\, t}$$

$$\cancel{E_1 A} - \bar{E}\cdot\langle\psi_1'|\bar{p}|\psi_2'\rangle B e^{-\frac{iE_2 t}{\hbar}} = \left(\frac{\partial A_1}{\partial t} + \cancel{E_1 A}\right)i\hbar\, e^{-iE_1/\hbar\, t}$$

and $$-e^{-\frac{iE_1 t}{\hbar}}\bar{E}\cdot\langle\psi_2'|\bar{p}|\psi_1'\rangle A = i\hbar\frac{\partial B}{\partial t}e^{-iE_2/\hbar\, t}$$

4) Because of 1) the second of these is the important one ($A \simeq$ const $\simeq 1$)

5) Thus from the top of the page ($A=1$) (sub for $\partial B/\partial t$)

$$\frac{\partial\langle\psi|p|\psi\rangle}{\partial t} \simeq -\frac{\overbrace{A^*A}^{1}}{i\hbar}\bar{E}\cdot\langle\psi_2'|\bar{p}|\psi_1'\rangle\langle\psi_1'|\bar{p}|\psi_2'\rangle$$

$$+ \text{c.c.} \quad + \frac{i}{\hbar}(E_1-E_2)\langle\psi|p|\psi\rangle$$

6) Assuming $E(t,\bar{r}) = E_0 e^{i(\omega t - i\bar{k}\cdot\bar{r})} + c.c.$ (4)
and we are at $\bar{r} = 0$ (and $k \ll 1/\text{size of atom}$)
use phasors to solve. Pick $e^{-i\omega t}$ term
(its resonant)

$$\frac{\partial}{\partial t}\langle\psi|p|\psi\rangle - \frac{i}{\hbar}(E_1 - E_2)\langle\psi|p|\psi\rangle$$
$$= -\frac{1}{i\hbar}\bar{E}_0^* \cdot \langle\psi_2'|\bar{p}|\psi_1'\rangle\langle\psi_1'|\bar{p}|\psi_2'\rangle e^{-i\omega t}$$

The L.H.S phasor terms are (from Eq. (3))

$$\frac{\partial}{\partial t}\left(A^*(t)\,B(t)\,\langle\psi_1'|p|\psi_2'\rangle\, e^{+i(E_1-E_2)/\hbar\, t}\right)$$

and thus the two L.H.S terms just become

$$\left(\frac{\partial}{\partial t}A^*(t)\,B(t)\right) e^{+i((E_1-E_2)/\hbar)t}$$ (which equals

from above) $= -\frac{1}{i\hbar}\bar{E}_0^* \cdot |\langle\psi_2'|\bar{p}|\psi_1'\rangle|^2 e^{-i(\omega t)}$

where for short hand write $|\langle\psi_2'|\bar{p}|\psi_1'\rangle|^2 = \langle\psi_2'|\bar{p}|\psi_1'\rangle\langle\psi_1'|\bar{p}|\psi_2'\rangle$ (and $E_{21} = E_2 - E_1$)

Thus $$\frac{\partial A^* B}{\partial t} = -\frac{1}{i\hbar}\bar{E}_0^* \cdot |\langle\psi_2'|\bar{p}|\psi_1\rangle|^2 e^{-i(\omega - E_{21}/\hbar)t}$$

And ($A^* B = 0$ at $t = 0$)

$$A^* B = -\frac{1}{i\hbar}\frac{1}{-i(\omega - E_{21}/\hbar)}\bar{E}_0^* \cdot |\langle\psi_2'|\bar{p}|\psi_1'\rangle|^2 e^{-i(\omega - \frac{E_{21}}{\hbar})t}$$

And thus the phasor $\langle\psi|p|\psi\rangle$ is

$$\langle\psi|\bar{p}|\psi\rangle = -\frac{|\langle\psi_2'|\bar{p}|\psi_1'\rangle|^2}{\hbar}\frac{e^{-i\omega t}}{(\omega - E_{21}/\hbar)} \cdot E_0 \quad \text{at } r = 0$$

The total $\langle\psi|\bar{p}|\psi\rangle$ is <u>this</u> + <u>c.c.</u> (resonant terms)

This is to be compared with the classical expression for the phasor solution ($E = E_0^* e^{-i\omega t}$)

$$(-\omega^2 + \Gamma(-i\omega) + \omega_0^2)\, \overbrace{q\bar{x}}^{\bar{p}} = \frac{q^2}{m} E_0^* e^{-i\omega t}$$

$$q\bar{x} = \bar{p} = \frac{q^2}{m} \frac{E_0^* e^{-i\omega t}}{(-\omega^2 + \omega_0^2 + \Gamma(-i\omega))}$$

$$\simeq \frac{q^2}{2m\omega_0} \frac{E_0^*}{(-\omega + \omega_0 - i\Gamma\omega_0)} e^{-i\omega t}$$

near resonance. With $\omega_0 = (E_2 - E_1)/\hbar$ neglecting Γ (damping), we see that to obtain the quantum result $\frac{q^2}{2m\omega_0}$ should be $\frac{|\bar{p}|^2}{\hbar}$ (where $\bar{p} = \langle \psi_2 | \bar{p} | \psi_1 \rangle$). This one can do by introducing $f = \frac{2m\omega_0 |\bar{p}|^2}{\hbar}$ into the classical oscillator equation