Lecture 19

Light-Matter Interaction and Optical Transitions – II Time-Dependent Perturbation Theory and Fermi's Golden Rule



Optical Transition to a Continuum of Final States



Energy Bands in Crystalline Solids

Silicon lattice

GaAs lattice

GaN lattice







Energy Bands in Crystalline Solids

Energy **Crystalline materials have electron energy eigenstates Energy band** distributed among different energy bands An energy band is a collection of energy eigenstates Bandgap whose energies are very close such that these energy eigenstates can be thought of as forming a <u>continuum</u> **Energy band** There are energy gaps between energy bands that Bandgap are called bandgaps **Energy band** Energy **Energy bands Conduction energy band (empty)** in Silicon Bandgap ~ 1.1 eV Valence energy band (full of electrons) Bandgap Core energy band (full of electrons)



Density of States (DOS) of Energy Bands

Consider a small interval ΔE of energy in an energy band at energy E

Question: How many energy eigenstates are in this energy interval?

Answer:

The number of energy eigenstates in a small energy interval ΔE equals:

$D(E) \Delta E$

The function D(E) is the density of states (DOS) function of the energy band

DOS function equals the number of energy eigenstates with energy *E* in an energy band per unit energy interval



Density of States (DOS) of Energy Bands and Counting

The number of energy eigenstates in a small energy interval ΔE centered around energy *E* equals:

 $D(E) \Delta E$

Suppose we need to count all the energy states between energy E_A and energy E_B , as shown

Energy *E*_B



Energy E_A

Answer:

 $\sum_{m} \{ \text{All levels with energy between } E_A \text{ and } E_B \}$ $= \int_{E_A}^{E_B} dE D(E)$



Light-Matter Interaction in Energy Bands

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Consider an electron in a solid subjected to a timedependent perturbation because light is passing through the solid

Question: What happens to this electron??

Assumption: The perturbation is weak

The Hamiltonian is:

$$\hat{H}(t) = \frac{\hat{p}^2}{2m} + V(\hat{\vec{r}}) - q\vec{E}(t).\,\hat{\vec{r}}$$

 $\dot{H}(\vec{r},t)$



Time-Dependent Perturbation Theory

Energy

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The full time-dependent Hamiltonian is:

 $\hat{H}(t) = \hat{H}_{o} + 2\hat{H}_{p}\cos(\omega t)$

Energy eigenstates:

$$\hat{H}_{\mathbf{o}} |\mathbf{e}_{j}\rangle = E_{j} |\mathbf{e}_{j}\rangle \qquad \qquad \sum_{j} |\mathbf{e}_{j}\rangle \langle \mathbf{e}_{j}| = \hat{\mathbf{1}}$$

$$\langle \mathbf{e}_{j} |\mathbf{e}_{k}\rangle = \delta_{jk}$$

$$\hat{H}(t) = \hat{1}\hat{H}(t)\hat{1}$$

$$= \left(\sum_{j} E_{j} |e_{j}\rangle\langle e_{j}|\right) + 2\cos(\omega t)\sum_{j,k} \langle e_{k} |\hat{H}_{p} |e_{j}\rangle |e_{k}\rangle\langle e_{j}|$$

$$\hat{H}_{o}$$
Matrix elements of the perturbing Hamiltonian
$$\langle e_{k} |\hat{H}_{p} |e_{j}\rangle = -\frac{qE_{o}d_{kj}}{2}$$

Time-Dependent Perturbation Theory Energy

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Need to solve:

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

Subject to the boundary condition: $|\psi(t=0)\rangle = |e_0\rangle$

Assume a solution of the form:

$$|\psi(t)\rangle = \sum_{j} c_{j}(t) e^{-i\frac{E_{j}}{\hbar}t} |e_{j}\rangle \xrightarrow{\text{Boundary} \\ \text{condition}} |\psi(t=0)\rangle = |e_{0}\rangle$$
$$\Rightarrow c_{j}(t=0) = \delta_{j0}$$

And plug into the Schrödinger equation:

$$\begin{split} i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle &= \hat{H}(t) |\psi(t)\rangle \\ \Rightarrow \sum_{j} \left[e^{-i\frac{E_{j}}{\hbar}t} i\hbar \frac{\partial c_{j}(t)}{\partial t} + E_{j}c_{j}(t) e^{-i\frac{E_{j}}{\hbar}t} \right] |e_{j}\rangle &= \left[\hat{H}_{o} + 2\cos(\omega t) \hat{H}_{p} \right] \sum_{j} c_{j}(t) e^{-i\frac{E_{j}}{\hbar}t} |e_{j}\rangle \\ \Rightarrow \sum_{j} \left[e^{-i\frac{E_{j}}{\hbar}t} i\hbar \frac{\partial c_{j}(t)}{\partial t} + E_{j}c_{j}(t) e^{-i\frac{E_{j}}{\hbar}t} \right] |e_{j}\rangle &= \sum_{j} E_{j}c_{j}(t) e^{-i\frac{E_{j}}{\hbar}t} |e_{j}\rangle \\ &+ 2\cos(\omega t) \sum_{j} c_{j}(t) e^{-i\frac{E_{j}}{\hbar}t} \hat{H}_{p} |e_{j}\rangle \end{split}$$

Time-Dependent Perturbation Theory

$$\sum_{j} \left[e^{-i\frac{E_{j}}{\hbar}t} i\hbar \frac{\partial c_{j}(t)}{\partial t} \right] \left| e_{j} \right\rangle = 2\cos(\omega t) \sum_{j} c_{j}(t) e^{-i\frac{E_{j}}{\hbar}t} \hat{H}_{p} \left| e_{j} \right\rangle$$

Multiply both sides from the left by $\langle \mathbf{e}_m |$ (where $m \neq 0$):

For times *t* not too large,

$$i\hbar \frac{\partial c_m(t)}{\partial t} = 2\cos(\omega t) \langle \mathbf{e}_m | \hat{H}_p | \mathbf{e}_0 \rangle \mathbf{e}^{-i\frac{(E_0 - E_m)}{\hbar}t}$$

$$\Rightarrow \frac{\partial \mathbf{c}_{m}(t)}{\partial t} = -\frac{i}{\hbar} \langle \mathbf{e}_{m} | \hat{\mathbf{H}}_{p} | \mathbf{e}_{0} \rangle \left[\mathbf{e}^{-i \frac{(\mathbf{E}_{0} + \hbar \omega - \mathbf{E}_{m})}{\hbar} t} + \mathbf{e}^{-i \frac{(\mathbf{E}_{0} - \hbar \omega - \mathbf{E}_{m})}{\hbar} t} \right]$$

This equation shows that the coefficient $c_m(t)$ is increasing with time!

 $\frac{|\mathbf{e}_0\rangle}{\hbar\omega}$ $\frac{|\mathbf{e}_0\rangle}{\hbar\omega}$ Boundary
condition $|\psi(t=0)\rangle = |\mathbf{e}_0\rangle$ $\Rightarrow \mathbf{c}_j(t=0) = \delta_{j0}$

Energy



The non-resonant term is oscillating fast as a function of time and will not contribute much if the RHS is integrated wrt time to get the coefficient $c_m(t)$

Therefore, we can write:

$$\frac{\partial \mathbf{c}_{m}(t)}{\partial t} = -\frac{i}{\hbar} \langle \mathbf{e}_{m} | \hat{\mathbf{H}}_{p} | \mathbf{e}_{0} \rangle \mathbf{e}^{-i\frac{(\mathbf{E}_{0} + \hbar\omega - \mathbf{E}_{m})}{\hbar}t}$$
Resonant term only

Time-Dependent Perturbation Theory: Upward Transitions Energy e_m) Now we integrate wrt time from *t*=0 to *t* : ħω e₀ $\frac{\partial \mathbf{c}_{m}(t)}{\partial t} = -\frac{i}{\hbar} \langle \mathbf{e}_{m} | \hat{\mathbf{H}}_{p} | \mathbf{e}_{0} \rangle \mathbf{e}^{-i \frac{(\mathbf{E}_{0} + \hbar \omega - \mathbf{E}_{m})}{\hbar} t}$ $\Rightarrow \boldsymbol{c}_{m}(t) = -\frac{i}{\hbar} \langle \boldsymbol{e}_{m} | \hat{\boldsymbol{H}}_{p} | \boldsymbol{e}_{0} \rangle \int_{0}^{t} dt' \boldsymbol{e}^{-i \frac{(\boldsymbol{E}_{0} + \hbar \boldsymbol{\omega} - \boldsymbol{E}_{m})}{\hbar} t'}$ $\Rightarrow c_{m}(t) = -\frac{i}{\hbar} \langle \mathbf{e}_{m} | \hat{H}_{p} | \mathbf{e}_{0} \rangle t \left| \frac{\sin \left[\frac{(E_{0} + \hbar \omega - E_{m})}{2\hbar} t \right]}{\frac{(E_{0} + \hbar \omega - E_{m})t}{2\hbar}} \right| \mathbf{e}^{-i \frac{(E_{0} + \hbar \omega - E_{m})}{2\hbar}t}$ $\Rightarrow \left| c_{m}(t) \right|^{2} = \frac{1}{\hbar^{2}} \left| \left\langle e_{m} \left| \hat{H}_{p} \right| e_{0} \right\rangle \right|^{2} t^{2} \left| \frac{\sin \left[\frac{\left(E_{0} + \hbar \omega - E_{m} \right)}{2\hbar} t \right]}{\frac{\left(E_{0} + \hbar \omega - E_{m} \right) t}{2\hbar}} \right|^{2}$



Time-Dependent Perturbation Theory: Upward Transition Rates Energy

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$$\Rightarrow \frac{d\left|c_{m}(t)\right|^{2}}{dt} = \frac{2\pi}{\hbar} \left|\left\langle \mathbf{e}_{m}\left|\hat{H}_{p}\right|\mathbf{e}_{0}\right\rangle\right|^{2} \delta\left(E_{0} + \hbar\omega - E_{m}\right)$$

 $\frac{d|c_m(t)|^2}{d|c_m(t)|^2}$ represents the rate of increase of the probability in the dt upper level m

The total transition rate for the electron to go to the higher energy states is given by:

$$R \uparrow = \sum_{m \neq 0} \frac{d |c_m(t)|^2}{dt} = \sum_{m \neq 0} \frac{2\pi}{\hbar} |\langle \mathbf{e}_m | \hat{H}_p | \mathbf{e}_0 \rangle|^2 \,\delta(E_0 + \hbar \omega - E_m) \qquad \text{Neplace summation} \\ = \int dE \, D(E) \,\frac{2\pi}{\hbar} |\langle \mathbf{e}_E | \hat{H}_p | \mathbf{e}_0 \rangle|^2 \,\delta(E_0 + \hbar \omega - E) \\ = D(E_0 + \hbar \omega) \,\frac{2\pi}{\hbar} |\langle \mathbf{e}_{E_0 + \hbar \omega} | \hat{H}_p | \mathbf{e}_0 \rangle|^2 \qquad \text{Fermi's Golden Rule}$$

Time-Dependent Perturbation Theory: Downward Transition Rates

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The **total** transition rate for the electron to go to the lower energy states is given by:

$$R \downarrow = \sum_{m \neq 0} \frac{d |c_m(t)|^2}{dt} = \sum_{m \neq 0} \frac{2\pi}{\hbar} |\langle \mathbf{e}_m | \hat{H}_p | \mathbf{e}_0 \rangle|^2 \delta (E_0 - \hbar \omega - E_m)$$
$$= \int dE D(E) \frac{2\pi}{\hbar} |\langle \mathbf{e}_E | \hat{H}_p | \mathbf{e}_0 \rangle|^2 \delta (E_0 - \hbar \omega - E)$$
$$= D(E_0 - \hbar \omega) \frac{2\pi}{\hbar} |\langle \mathbf{e}_{E_0 - \hbar \omega} | \hat{H}_p | \mathbf{e}_0 \rangle|^2 \qquad \text{Fermi's Golden Rule}$$
$$\oint DOS \text{ evaluated at the electron final energy}$$

Exponential Decay of the Initial State Energy

With little extra work one can also find out how the probability of the electron being in the initial state is behaving with time:

$$\frac{d\left|c_{0}\left(t\right)\right|^{2}}{dt}=-\left(R\uparrow+R\downarrow\right)\left|c_{0}\left(t\right)\right|^{2}$$

Solution, subject to the boundary condition $c_0(t=0)=1$, is:

$$\left|c_{0}(t)\right|^{2}=e^{-\left(R\uparrow+R\downarrow\right)t}$$

The probability of the electron being in the initial state decays exponentially with time and the decay constant is related to the transition rates to the higher and lower energy states

Notice also the probability conservation:

$$\frac{d\left|c_{0}\left(t\right)\right|^{2}}{dt} + \sum_{\substack{m\neq0}} \frac{d\left|c_{m}\left(t\right)\right|^{2}}{dt} = 0$$
$$\Rightarrow \left|c_{0}\left(t\right)\right|^{2} + \sum_{\substack{m\neq0}} \left|c_{m}\left(t\right)\right|^{2} = 1$$

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Optical Transition Rates: Fermi's Golden Rule
Stimulated Absorption of Light by an Electron:

$$R \uparrow = \sum_{m} \frac{2\pi}{\hbar} |\langle \mathbf{e}_{m} | \hat{H}_{p} | \mathbf{e}_{0} \rangle|^{2} \delta(E_{0} + \hbar \omega - E_{m})$$

$$= D(E_{0} + \hbar \omega) \frac{2\pi}{\hbar} |\langle \mathbf{e}_{E_{0} + \hbar \omega} | \hat{H}_{p} | \mathbf{e}_{0} \rangle|^{2}$$

$$= D(E_{0} + \hbar \omega) \frac{2\pi}{\hbar} |\frac{qE_{0}d}{2}|^{2}$$

$$\overrightarrow{H}(\vec{r}, t)$$

Stimulated Emission of Light by an Electron:

$$R \downarrow = \sum_{m} \frac{2\pi}{\hbar} \left| \left\langle \mathbf{e}_{m} \left| \hat{H}_{p} \right| \mathbf{e}_{0} \right\rangle \right|^{2} \delta \left(E_{0} - \hbar \omega - E_{m} \right)$$
$$= D \left(E_{0} - \hbar \omega \right) \frac{2\pi}{\hbar} \left| \left\langle \mathbf{e}_{E_{0} - \hbar \omega} \left| \hat{H}_{p} \right| \mathbf{e}_{0} \right\rangle \right|^{2}$$
$$= D \left(E_{0} - \hbar \omega \right) \frac{2\pi}{\hbar} \left| \frac{q E_{0} d}{2} \right|^{2}$$

d = dipole matrix element between the initial and final states of the electron

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Stimulated Emission

Light Absorption in Crystalline Solids

Bands in GaAs in thermal equilibrium



Light Amplification by Stimulated Emission of Radiation (LASER)





Energy

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We start from the general equation derived earlier:

$$\sum_{j} \left[\mathbf{e}^{-i\frac{\mathbf{E}_{j}}{\hbar}t} i\hbar \frac{\partial \mathbf{c}_{j}(t)}{\partial t} \right] \left| \mathbf{e}_{j} \right\rangle = 2\cos(\omega t) \sum_{j} \mathbf{c}_{j}(t) \mathbf{e}^{-i\frac{\mathbf{E}_{j}}{\hbar}t} \hat{H}_{p} \left| \mathbf{e}_{j} \right\rangle$$

Multiply both sides from the left by $\langle \mathbf{e}_m |$ (where $m \neq 0$):

$$\frac{\partial \mathbf{c}_{m}(t)}{\partial t} = -\frac{i}{\hbar} \langle \mathbf{e}_{m} | \hat{H}_{p} | \mathbf{e}_{0} \rangle \left[\mathbf{e}^{-i \frac{(\mathbf{E}_{0} + \hbar \omega - \mathbf{E}_{m})}{\hbar} t} + \mathbf{e}^{-i \frac{(\mathbf{E}_{0} - \hbar \omega - \mathbf{E}_{m})}{\hbar} t} \right] \mathbf{c}_{0}(t) \quad \longrightarrow (1)$$

Multiply both sides from the left by $\langle e_0 |$ in the general equation to get:

$$\frac{\partial c_{0}(t)}{\partial t} = \sum_{m \neq 0} -\frac{i}{\hbar} \langle \mathbf{e}_{0} | \hat{H}_{p} | \mathbf{e}_{m} \rangle \left[\mathbf{e}^{-i \frac{(E_{m} + \hbar \omega - E_{0})}{\hbar} t} + \mathbf{e}^{-i \frac{(E_{m} - \hbar \omega - E_{0})}{\hbar} t} \right] c_{m}(t) \longrightarrow (2)$$

Now we will solve (1) and stick its solution in (2)

Appendix: Absence of Rabi Oscillations in Transitions to a Continuum Energy Solution of (1) by direct integration is: $c_{m}(t) = -\frac{i}{\hbar} \langle \mathbf{e}_{m} | \hat{H}_{p} | \mathbf{e}_{0} \rangle_{0}^{t} dt' \left[\mathbf{e}^{-i\frac{(E_{0}+\hbar\omega-E_{m})}{\hbar}t'} + \mathbf{e}^{-i\frac{(E_{0}-\hbar\omega-E_{m})}{\hbar}t'} \right] c_{0}(t')$ Substitute the above in (2) to get (and ignoring some unimportant terms): $\frac{\partial c_{0}(t)}{\partial t} = -\sum_{m \neq 0} \frac{1}{\hbar^{2}} |\langle \mathbf{e}_{0} | \hat{H}_{p} | \mathbf{e}_{m} \rangle|^{2} \int_{0}^{t} dt' \left[\mathbf{e}^{-i\frac{(E_{m}+\hbar\omega-E_{0})}{\hbar}(t-t')} + \mathbf{e}^{-i\frac{(E_{m}-\hbar\omega-E_{0})}{\hbar}(t-t')} \right] c_{0}(t')$

The above is an equation for $c_0(t)$ alone!

Now change the order of time integration and summation over "m" and then convert the summation into an integral over energy using the density of states D(E):

$$\frac{\partial c_{0}(t)}{\partial t} = -\int_{0}^{t} dt \int dE D(E) \frac{1}{\hbar^{2}} \left| \left\langle e_{0} \left| \hat{H}_{p} \right| e_{E} \right\rangle \right|^{2} \left[e^{-i \frac{(E + \hbar\omega - E_{0})}{\hbar}(t - t')} + e^{-i \frac{(E - \hbar\omega - E_{0})}{\hbar}(t - t')} \right] c_{0}(t')$$

$$\frac{\partial c_{0}(t)}{\partial t} = -\int_{0}^{t} dt' \left[\int dE D(E) \frac{1}{\hbar^{2}} \left| \left\langle \mathbf{e}_{0} \right| \hat{H}_{p} \left| \mathbf{e}_{E} \right\rangle \right|^{2} e^{-i \frac{(E+\hbar\omega-E_{0})}{\hbar}(t-t')} + \int dE D(E) \frac{1}{\hbar^{2}} \left| \left\langle \mathbf{e}_{0} \right| \hat{H}_{p} \left| \mathbf{e}_{E} \right\rangle \right|^{2} e^{-i \frac{(E-\hbar\omega-E_{0})}{\hbar}(t-t')} \right] c_{0}(t')$$

Note that the integration over time implies that in the first term (or second term) inside the brackets, energies that matter are those for which $E = E_0 - \hbar \omega (\text{or } E = E_0 + \hbar \omega)$

So if D(E) and $|\langle e_0 | \hat{H}_p | e_E \rangle|$ are not strong functions of energy around the energies $E = E_0 \pm \hbar \omega$ then one may write:

$$\frac{\partial c_{0}(t)}{\partial t} = -\frac{1}{\hbar^{2}}\int_{0}^{t} dt' \begin{bmatrix} D(E_{0} - \hbar\omega) \left| \left\langle e_{0} \right| \hat{H}_{p} \left| e_{E_{0} - \hbar\omega} \right\rangle \right|^{2} \int dE \ e^{-i\frac{(E + \hbar\omega - E_{0})}{\hbar}(t - t')} \\ + D(E_{0} + \hbar\omega) \left| \left\langle e_{0} \right| \hat{H}_{p} \left| e_{E_{0} + \hbar\omega} \right\rangle \right|^{2} \int dE \ e^{-i\frac{(E - \hbar\omega - E_{0})}{\hbar}(t - t')} \end{bmatrix} c_{0}(t')$$

$$\frac{\partial c_{0}(t)}{\partial t} = -\frac{1}{\hbar^{2}} \int_{0}^{t} dt' \left[D\left(E_{0} - \hbar\omega\right) \left| \left\langle e_{0} \right| \hat{H}_{p} \left| e_{E_{0} - \hbar\omega} \right\rangle \right|^{2} \int dE \ e^{-i \frac{\left(E - \hbar\omega - E_{0}\right)}{\hbar} \left(t - t'\right)} + D\left(E_{0} + \hbar\omega\right) \left| \left\langle e_{0} \right| \hat{H}_{p} \left| e_{E_{0} + \hbar\omega} \right\rangle \right|^{2} \int dE \ e^{-i \frac{\left(E - \hbar\omega - E_{0}\right)}{\hbar} \left(t - t'\right)} \right] c_{0}(t')$$

Now note that:

$$\int dE \, e^{-i \frac{\left(E \pm \hbar \omega - E_0\right)}{\hbar} \left(t - t'\right)} = 2\pi \hbar \delta \left(t - t'\right) \quad \longrightarrow \quad (3)$$

Carry out the time integrations and use (3) to get:

$$\frac{\partial c_{0}(t)}{\partial t} = -\left[\frac{\pi}{\hbar}D(E_{0}-\hbar\omega)\Big|\langle e_{0}\Big|\hat{H}_{p}\Big|e_{E_{0}-\hbar\omega}\Big|^{2} + \frac{\pi}{\hbar}D(E_{0}+\hbar\omega)\Big|\langle e_{0}\Big|\hat{H}_{p}\Big|e_{E_{0}+\hbar\omega}\Big|^{2}\right]c_{0}(t)$$
$$= -\frac{1}{2}(R_{\downarrow}+R_{\uparrow})c_{0}(t)$$

$$\frac{\partial c_{0}(t)}{\partial t} = -\frac{1}{2} \left(R_{\downarrow} + R_{\uparrow} \right) c_{0}(t)$$

Which implies:

$$\frac{\partial \left| \boldsymbol{c}_{0}\left(t \right) \right|^{2}}{\partial t} = - \left(\boldsymbol{R}_{\downarrow} + \boldsymbol{R}_{\uparrow} \right) \left| \boldsymbol{c}_{0}\left(t \right) \right|^{2}$$



This shows that the probability of the electron remaining in the initial state decays exponentially and does not exhibit any Rabi oscillations!

So why do we not see Rabi oscillations? Why doesn't $c_0(t)$ become large ever again? The answer lies in these two equations we had written down earlier:

$$\frac{\partial \mathbf{c}_{m}(t)}{\partial t} = -\frac{i}{\hbar} \langle \mathbf{e}_{m} | \hat{H}_{p} | \mathbf{e}_{0} \rangle \left[\mathbf{e}^{-i \frac{(E_{0} + \hbar\omega - E_{m})}{\hbar} t} + \mathbf{e}^{-i \frac{(E_{0} - \hbar\omega - E_{m})}{\hbar} t} \right] \mathbf{c}_{0}(t) \qquad \longrightarrow (1)$$

$$\frac{\partial \mathbf{c}_{0}(t)}{\partial t} = \sum_{m \neq 0} -\frac{i}{\hbar} \langle \mathbf{e}_{0} | \hat{H}_{p} | \mathbf{e}_{m} \rangle \left[\mathbf{e}^{-i \frac{(E_{m} + \hbar\omega - E_{0})}{\hbar} t} + \mathbf{e}^{-i \frac{(E_{m} - \hbar\omega - E_{0})}{\hbar} t} \right] \mathbf{c}_{m}(t) \qquad \longrightarrow (2)$$

Because different energy levels E_m have different detunings $(E_m \mp \hbar \omega + E_0)$, different coefficients $c_m(t)$ acquire different relative phases by (1). Consequently, they interfere destructively in (2) and, therefore, $c_0(t)$ never gets regenerated after it has decreased from its initial value