Applying time-dependent perturbation theory
Absorption

Now consider only the case associated with absorption
presuming we are starting in a lower energy state
and transitioning to a higher energy one
(The treatment of the stimulated emission case is
essentially identical
with the energies of the states reversed)

Then we have

\[ P(j) \approx \frac{t_o^2}{\hbar^2} \left| \langle \psi_j | \hat{H}_{po} | \psi_m \rangle \right|^2 \left\{ \frac{\sin \left[ \left( \omega_{jm} - \omega \right) t_o / 2 \right]}{\left( \omega_{jm} - \omega \right) t_o / 2} \right\}^2 \]
Absorption

Analyzing the case of a transition between one state and exactly one other state using this approach has some formal difficulties as we let the time $t_o$ become arbitrarily large. The sinc squared term becomes arbitrarily sharp in $\omega$. Unless the frequency is exactly correct, we will get no absorption.

We can solve this problem with more sophisticated analysis specifically, the use of density matrices which allow “widths” to the absorption lines.
Lorentzian line shape

With density matrices, we end up replacing the sinc squared function with a Lorentzian line with angular frequency half-width $1/T_2$ where $T_2$ is the time between scatterings, e.g., collisions with other atoms.
Lorentzian line shape

We can rationalize this based on an energy-time uncertainty relation. If the system only exists in its original form for a time $T_2$, then we should expect that the energy of the transition is only defined in energy to $\sim \pm \hbar / T_2$ or in $\omega$ to $\sim \pm 1 / T_2$. 

\[
\frac{1}{1 + (\omega - \omega_o)^2 T_2^2}
\]
Dense sets of possible transitions

A major class of problems can, however, be analyzed using our approach.

Suppose we have not one possible transition with energy difference $\hbar \omega_{jm}$
but a dense of transitions near the photon energy $\hbar \omega$
all with essentially identical matrix elements.

This kind of situation occurs routinely in solids.
Dense sets of possible transitions

We presume that this set of possible transitions is very dense with a density $g_J(\hbar\omega)$ per unit energy near the photon energy $\hbar\omega$ giving $g_J(\hbar\omega)\Delta E$ transitions within energy range $\Delta E$

$g_J(\hbar\omega)$ is sometimes known as a “joint density of states” since it refers to transitions between states
Absorption into dense sets of possible transitions

Then adding up the probabilities for absorbing transitions
we obtain a total probability of absorption by this set of transitions of

\[ P_{\text{tot}} \approx \frac{t_o^2}{\hbar^2} \left| \langle \psi_j | \hat{H}_{po} | \psi_m \rangle \right|^2 \int \sin\left[ \frac{(\omega_{jm} - \omega)t_o}{2} \right]^2 \left[ \frac{\omega_{jm} - \omega}{t_o / 2} \right] g_j(\hbar \omega_{jm}) d\hbar \omega_{jm} \]

\( g_j(\hbar \omega_{jm}) \) is presumed constant over small energy ranges and the sinc squared term is presumed narrow in \( \omega_{jm} \) hence we can take \( g_j(\hbar \omega_{jm}) \) out of the integral as \( g_j(\hbar \omega) \)
Absorption into dense sets of possible transitions

Formally changing the variable in the integral to

\[ x = \left( \omega_{jm} - \omega \right) t_o / 2 \]

gives

\[ P_{tot} \approx \frac{t_o^2}{\hbar^2} \left| \langle \psi_j | \hat{H}_{po} | \psi_m \rangle \right|^2 \frac{2\hbar}{t_o} g_j (\hbar \omega) \int \left[ \frac{\sin x}{x} \right]^2 dx \]

Using the mathematical result

\[ \int_{-\infty}^{\infty} \left( \frac{\sin x}{x} \right)^2 dx = \pi \]

we obtain

\[ P_{tot} \approx \frac{2\pi t_o}{\hbar} \left| \langle \psi_j | \hat{H}_{po} | \psi_m \rangle \right|^2 g_j (\hbar \omega) \]
Fermi’s Golden Rule

Now we see that we have a total probability of making some transition that is proportional to the time $t_o$ that the perturbation is turned on. This allows us now to deduce a transition rate or, here, a rate of absorption of photons

$$W = \frac{2\pi}{\hbar} \left| \langle \psi_j | \hat{H}_{po} | \psi_m \rangle \right|^2 g_J (\hbar \omega)$$
Fermi’s Golden Rule

This result

\[ W = \frac{2\pi}{\hbar} \left| \langle \psi_j | \hat{H}_{po} | \psi_m \rangle \right|^2 g_J (\hbar \omega) \]

is known as “Fermi’s Golden Rule”

It is one of the most useful results of time-dependent perturbation theory

and forms the basis for calculation of, for example, the optical absorption spectra of solids

and to many other problems involving simple harmonic perturbations
Fermi’s Golden Rule – alternative statement

This rule is also stated

\[ w_{jm} = \frac{2\pi}{\hbar} \left| \langle \psi_j | \hat{H}_{po} | \psi_m \rangle \right|^2 \delta(E_{jm} - \hbar \omega) \]

where \( w_{jm} \) is the transition rate
between the specific states \( |\psi_m\rangle \) and \( |\psi_j\rangle \)
and \( \delta(E_{jm} - \hbar \omega) \) is the Dirac delta function
an infinitely high and sharp unit-area “spike”
at \( E_{jm} = \hbar \omega \)

The total transition rate involving all the possible similar transitions in the neighborhood is then formally

\[ W = \int w_{jm} g_J (\hbar \omega_{jm}) d\hbar \omega_{jm} \]
Applying time-dependent perturbation theory

Refractive index
Refractive index

In classical electromagnetism, when we apply an electric field $E$ to a material, we can imagine that the field pulls the average position of the negatively charged electrons away from the average position of the positively charged nuclei of the atoms, creating what is called a "polarization" $P$. 
Refractive index

At least for applied fields that are small compared to the fields in the atoms
we would expect that this “polarization” $P$

is proportional to the applied field $E$

with a proportionality constant
the “susceptibility” $\chi$

For historical reasons

a fundamental constant is also involved
the “electric constant” $\varepsilon_0$

so we write $P = \varepsilon_0 \chi E$
Refractive index

In a classical view of electromagnetic waves
the fact that we are moving these electrons
with the oscillating field
means that we have a new oscillating current
which itself generates new waves
These new waves interfere with the original waves
with the net result that the effective (phase) velocity of the total wave is changed
formally, divided by the “refractive index” $n_r$
Refractive index

If we follow through the classical electromagnetism of this problem for example, using Maxwells’ equations we can conclude at least for non-absorbing materials that the refractive index is given by

$$n_r = \sqrt{1 + \chi}$$

Hence, if we can calculate the proportionality between $P$ and $E$ we can calculate $n_r$. 
Calculation of refractive index

Consider a system with a single electron
or in which our interactions are only with a single electron

Classically the dipole moment $\mu_{\text{dip}}$
associated with moving a single electron through a distance $z$ is
by definition

$$\mu_{\text{dip}} = -ez$$

where the minus sign is because the electron charge is negative
Calculation of refractive index

The polarization $P$ is formally the dipole moment per unit volume and so the quantum mechanical expectation value of the polarization is

$$\langle P \rangle = \frac{-e \langle z \rangle}{V}$$

where $V$ is the volume of the system.

Our quantum mechanical task of calculating refractive index reduces essentially to calculating $\langle P \rangle$. 
Calculation of refractive index

Since we are working in first-order perturbation theory, we write the (approximate) total state of the system:

\[
|\Psi\rangle = |\Phi^{(0)}\rangle + |\Phi^{(1)}\rangle
\]

Note we use the full time-dependent state vectors (kets):

- \( |\Phi^{(0)}\rangle \) is the unperturbed state vector
- \( |\Phi^{(1)}\rangle \) is the first-order (time-dependent) correction

where

\[
|\Phi^{(1)}\rangle = \sum_n a_n^{(1)}(t) \exp(-i\omega_n t) |\psi_n\rangle
\]

with unperturbed energy eigenvalues \( E_n \) and eigenfunctions \( |\psi_n\rangle \).
Calculation of refractive index

With the state vector $|\Psi\rangle = |\Phi^{(0)}\rangle + |\Phi^{(1)}\rangle$

the expectation value of the polarization would be

$$\langle P \rangle = -\frac{e}{V} \langle \Psi \mid z \mid \Psi \rangle$$

$$= -\frac{e}{V} \left[ \langle \Phi^{(0)} \mid z \mid \Phi^{(0)} \rangle + \langle \Phi^{(1)} \mid z \mid \Phi^{(0)} \rangle + \langle \Phi^{(0)} \mid z \mid \Phi^{(1)} \rangle + \langle \Phi^{(1)} \mid z \mid \Phi^{(1)} \rangle \right]$$

The first term $-e \langle \Phi^{(0)} \mid z \mid \Phi^{(0)} \rangle$

is just the static dipole moment of the material in its unperturbed state

so we will not consider it further
Calculation of refractive index

\[ \langle P \rangle = -\frac{e}{V} \langle \Psi | z | \Psi \rangle \]

\[ = -\frac{e}{V} \left[ \langle \Phi^{(0)} | z | \Phi^{(0)} \rangle + \langle \Phi^{(1)} | z | \Phi^{(0)} \rangle + \langle \Phi^{(0)} | z | \Phi^{(1)} \rangle + \langle \Phi^{(1)} | z | \Phi^{(1)} \rangle \right] \]

The fourth term \( -e \langle \Phi^{(1)} | z | \Phi^{(1)} \rangle \)

is second order in the perturbation

and hence, in this first order calculation

we drop it also
Calculation of refractive index

So we are left with

\[
\langle P \rangle = -\frac{e}{V} \left[ \langle \Phi^{(1)} | z | \Phi^{(0)} \rangle + \langle \Phi^{(0)} | z | \Phi^{(1)} \rangle \right]
\]

But because \( z \) is a Hermitian operator

\[
\langle \Phi^{(1)} | z | \Phi^{(0)} \rangle = \langle \Phi^{(0)} | z | \Phi^{(1)} \rangle^*
\]

therefore

\[
\langle P \rangle = -\frac{2e}{V} \text{Re} \left[ \langle \Phi^{(0)} | z | \Phi^{(1)} \rangle \right]
\]
Calculation of refractive index

For the sake of definiteness
we presume we start in eigenstate $m$, i.e.,

$$\left| \Phi^{(0)} \right\rangle = \exp(-i\omega_m t)|\psi_m\rangle$$

Hence, using the first-order perturbation expansion

$$\left| \Phi^{(1)} \right\rangle = \sum_n a_n^{(1)}(t)\exp(-i\omega_n t)|\psi_n\rangle$$

then, from

$$\langle P \rangle = -\frac{2e}{V} \text{Re} \left[ \langle \Phi^{(0)} | z | \Phi^{(1)} \rangle \right]$$

we have

$$\langle P \rangle = -\frac{2e}{V} \text{Re} \left[ \sum_n a_n^{(1)}(t)\exp(i\omega_{mn} t)|\psi_m\rangle z |\psi_n\rangle \right]$$
Calculation of refractive index

We are interested here in the steady-state situation with a continuous oscillating field so we take

\( \hat{H}_p (t) = eE(t) z = \hat{H}_{po} \left[ \exp(-i\omega t) + \exp(i\omega t) \right] \)

as valid for all times.

We can rewrite \( \dot{\alpha}_q^{(1)}(t) = \frac{1}{i\hbar} \exp(i\omega_{qm}t) \left\langle \psi_q \right| \hat{H}_p (t) \left| \psi_m \right\rangle \) as

\[ \dot{\alpha}_q^{(1)}(t) = \frac{eE_o}{i\hbar} \left\langle \psi_q \right| z \left| \psi_m \right\rangle \exp(i\omega_{qm}t) \left[ \exp(-i\omega t) + \exp(i\omega t) \right] \]

to obtain

\[ \alpha_q^{(1)}(t) = -\frac{eE_o}{\hbar} \left\langle \psi_q \right| z \left| \psi_m \right\rangle \left[ \exp\left[ i \left( \omega_{qm} - \omega \right) t \right] \frac{1}{(\omega_{qm} - \omega)} + \exp\left[ i \left( \omega_{qm} + \omega \right) t \right] \frac{1}{(\omega_{qm} + \omega)} \right] \]
Calculation of refractive index

Substituting

$$a_q^{(1)}(t) = -\frac{eE_o}{\hbar} \langle \psi_q | z | \psi_m \rangle \left[ \frac{\exp[i(\omega_{qm} - \omega)t]}{(\omega_{qm} - \omega)} + \frac{\exp[i(\omega_{qm} + \omega)t]}{(\omega_{qm} + \omega)} \right]$$

into

$$\langle P \rangle = -\frac{2e}{V} \text{Re} \left[ \sum_n a_n^{(1)}(t) \exp(i\omega_{mn}t) \langle \psi_m | z | \psi_n \rangle \right]$$

gives

$$\langle P \rangle = \frac{2e^2E_o}{\hbar V} \text{Re} \sum_n |\langle \psi_m | z | \psi_n \rangle|^2 \exp(i\omega_{mn}t) \left[ \frac{\exp[i(\omega_{nm} - \omega)t]}{(\omega_{nm} - \omega)} + \frac{\exp[i(\omega_{nm} + \omega)t]}{(\omega_{nm} + \omega)} \right]$$
Calculation of refractive index

Noting $\omega_{mn} = -\omega_{nm}$ and taking the real part gives

$$\langle P \rangle = \frac{2e^2 E_o}{\hbar V} \sum_n |\langle \psi_m | z | \psi_n \rangle|^2 \left[ \frac{\cos(-\omega t)}{(\omega_{nm} - \omega)} + \frac{\cos(\omega t)}{(\omega_{nm} + \omega)} \right]$$

$$= \frac{2e^2 E_o \cos(\omega t)}{\hbar V} \sum_n |\langle \psi_m | z | \psi_n \rangle|^2 \left[ \frac{1}{(\omega_{nm} - \omega)} + \frac{1}{(\omega_{nm} + \omega)} \right]$$

and so we have, from $P = \varepsilon_o \chi E$

$$\chi = \frac{e^2}{\varepsilon_o \hbar V} \sum_n |\langle \psi_m | z | \psi_n \rangle|^2 \left[ \frac{1}{(\omega_{nm} - \omega)} + \frac{1}{(\omega_{nm} + \omega)} \right]$$
Calculation of refractive index

From \( \chi = \frac{e^2}{\varepsilon_0 \hbar V} \sum_n |\langle \psi_m | z | \psi_n \rangle|^2 \left[ \frac{1}{(\omega_{nm} - \omega)} + \frac{1}{(\omega_{nm} + \omega)} \right] \)

and using \( n_r = \sqrt{1 + \chi} \)

we can now deduce the refractive index \( n_r \)

completing our calculation of refractive index

Hence, knowing the unperturbed energy eigenfunctions and eigenvalues for some quantum mechanical system we can calculate the refractive index using time-dependent perturbation theory.
Absorption and refractive index

Note a key difference between absorption and refractive index.

For absorption, the frequency $\omega$ must match the transition frequency $\omega_{nm}$ very closely for that particular transition to give rise to absorption of photons.
Absorption and refractive index

For the refractive index

the contribution of a particular possible transition $|\psi_m\rangle \rightarrow |\psi_n\rangle$

to the susceptibility

and hence to the refractive index

is finite

even when the frequencies do not match exactly or even closely

That contribution to the susceptibility rises steadily as $\omega$ rises towards $\omega_{nm}$
Absorption and refractive index

Note that
if we have an absorbing transition at some frequency $\omega_{nn}$
it contributes to refractive index at all frequencies

Refractive index (in a region where the material is transparent)
arises entirely because of the possibility of absorption at other frequencies

If there is a refractive index different from unity
then there must be absorption possible at some other frequency or frequencies
Absorption and refractive index

The relation between refractive index and absorption is known from classical physics through the Kramers-Kronig relations. The derivation of those relations is entirely mathematical, shedding no light on the physical mechanism whereby absorption and refractive index are related.
Absorption and refractive index

With our quantum mechanical expressions we can understand any particular aspect in the relation between the two processes.

In the quantum mechanical picture, we find even though we are in a transparent spectral region there are finite occupation probabilities for all of the states of the system which are essential if the material has a polarization.
Absorption and refractive index

The polarization arises because the charges in the material change their physical wavefunctions in response to the field, mixing in other states of the system in response to the perturbation.

If we examined the expectation value of the energy of the material, we would also find quite real energy stored in the material as a result, even though the material is transparent.