\[
(Z-E_n) \langle n | G(z) | i \rangle = \langle n | V G(z) | i \rangle \\
\quad \downarrow \\
\text{desired M.E.}
\]

Now insert \( P+Q \) between \( V \) and \( G(z) \) on the RHS, where \( P = |i\rangle \langle i | \) and \( Q = 1-P \):

\[
\langle n | V G(z) | i \rangle = \langle n | V l | i \rangle \langle i | G(z) | l \rangle + \langle n | V Q G(z) | l \rangle
\]

\[
\rightarrow \text{this is } \frac{1}{D(z)}.
\]

The diagonal M.E. of \( G(z) \) appears in the first term. The 2nd term is actually \( \Theta(V^2) \) as we see by using the L.S eqn for \( G(z) \),

\[
G(z) = G_0(z) + G_0(z) V G(z),
\]

\[
\langle n | V Q G(z) | l \rangle = \langle n | V Q G_0(z) | l \rangle + \langle n | V Q G_0(z) V G(z) | l \rangle.
\]

The first term vanishes since \( Q \) and \( G_0(z) \) commute, and since \( Q |i\rangle = 0 \). The 2nd term is \( \Theta(V^2) \), as claimed. So, dividing by \( Z-E_n \), we have

\[
\langle n | G(z) | i \rangle = \frac{\langle n | V | i \rangle}{(Z-E_n)D(z)} + \Theta(V^2).
\]

Neglecting the \( \Theta(V^2) \) term, we have
\[ a_n(t) = \frac{-1}{2\pi i} \int_{C_+} dz \frac{e^{-izt}}{(z-E_n)D(z)} \langle n|\psi|l\rangle \]

Closing the contour we pick up two poles, one at \( z=E_n \), the other at \( z=i\tilde{E}_i - i\Gamma/2 \). By the residue theorem we find

\[ a_n(t) = \left( \frac{e^{-iE_nt}}{D(E_n)} + \frac{e^{-i\tilde{E}_i t - i\Gamma t/2}}{\tilde{E}_i - i\Gamma/2 - E_n} \right) \langle n|\psi|l\rangle \]

If we neglect \( O(v) \) and \( O(v^2) \) terms in the exponent and denominator, we get the same answer as 1st order TDPT. But this answer is valid for longer times.

In the limit \( t \gg \tau \) the second term goes away and we have

\[ a_n(t) = \frac{e^{-iE_nt}}{D(E_n)} \langle n|\psi|l\rangle \quad \text{or} \quad c_n(t) = \frac{1}{D(E_n)} \langle n|\psi|l\rangle. \]
At long times \((t \gg \tau)\) the transition amplitudes in the interaction picture are constant, which means that the system is evolving according to \(H_0\) (the term \(V\) is having no effect). (This is because the Sch. Eqn. in the interaction picture is
\[
\frac{\partial}{\partial t} |\psi_+(t)\rangle = V_+(t) |\psi_+(t)\rangle.
\]

The physical reason for this is that when \(t \gg \tau\) the atom has dropped completely into the lower state \(A\) and the photons have long since departed and are moving away at the speed of light and no longer interacting with the system.

BTW you may wonder why in the formula for \(A_n(t)\) we see the phase \(e^{-iE_n t - \Gamma t/2}\) for the initial state, but only \(e^{iE_n t}\) for the final state. Shouldn't the final state energy \(E_n\) also be corrected for the real and imaginary parts of its energy shift, that is, shouldn't we see \(E_n - i \Gamma n/2\) ? The answer is yes, and if we had carried the expansion of \(\langle n|\mathbf{G}(t)|1\rangle\) to higher order we would see these corrections appear. For simplicity we have assumed that the final state \(|n\rangle\) in question belong to the ground state of the atom, so \(\Gamma_n = 0\), and we have ignored the small shifts \(\Delta E_n^{(1)}\) and \(\Delta E_n^{(2)}\).
If the initial atomic state $\Psi$ can make transitions to several lower states $|A_1\rangle, |A_2\rangle, \ldots$, not all of which are the ground state, then we have a compound decay process that requires a more complicated analysis.

Now let's look at energy conservation in the decay, that is, let's ask to what extent the energy $E_n$ of the final state is equal to the energy of the initial state. Obviously the transition amplitude $C_n$ is largest when the denominator $D(E_n)$ is small, and

$$D(E_n) = E_n - E_i - \langle i|V|i\rangle - \sum_{k\neq i} \left( \frac{\mathbf{P}}{E_n - E_k} \right) |k\rangle \langle k|^* + \sum_{k\neq i} \delta(E_n - E_k) |k\rangle \langle k|^*$$

Obviously the denominator is small when $E_n \approx E_i$, and in that case we can replace the $E_n$ in the 2nd order terms by $E_i$, whereupon

$$D(E_n) = E_n - E_i + i\Gamma/2.$$

So for the final states with $E_n \approx E_i$, the only ones to receive a significant final amplitude, we have

$$C_n(t) = \frac{\langle n|V|i\rangle}{E_n - E_i + i\Gamma/2}.$$
Squaring this we get the probability,

\[ P_n(t) = \frac{1}{(E_n - \tilde{E}_i)^2 + \Gamma^2/4} \left| \langle n \mid \gamma \mid i \rangle \right|^2. \]

That's it.

The prefactor is a Lorentzian function. Regarded as a function of the final energy \( E_n \) (for fixed initial state \( |i\rangle \)) it looks like this:

\[ \text{Lorentzian} \]

\[ \Gamma = \text{FWHM} \]

\[ E_n \]

\[ \tilde{E}_i \]

Recall that for \( E_1 \) optical transitions in atoms (in a.u.) \( \Gamma = O(a^3) \), \( a^3 \approx 10^{-6} \), so on the atomic scale this Lorentzian is very narrow and looks like a \( \delta \)-fn if integrated against a function of energy that is slowly varying on the scale of \( \Gamma \). In fact, using

\[ \lim_{a \to 0} \frac{a}{x^2 + a^2} = \pi \delta(x), \]

we have

\[ P_n(t) = \frac{2\pi}{\Gamma} \delta(E_n - \tilde{E}_i) \left| \langle n \mid \gamma \mid i \rangle \right|^2 \]

assuming the width of the Lorentzian is too small to matter.
Summing this over \( n \) and using the defn of \( \Gamma \), we get

\[
\sum_{n \neq i} P_n(t) = \frac{2\pi}{\Gamma} \sum_{n \neq i} \delta(E_n - \tilde{E}_i) |\langle n | V | i \rangle|^2 = 1
\]

(ignoring the small diff. betw. \( E_i \) and \( \tilde{E}_i \)). At large \( t \gg \tau \), the prob. of not finding the system in state \( |i\rangle \) is 1, as it must be.

The Lorentzian gives the experimental distribution of photon energies observed in the decay of an excited state, if other effects that broaden spectral lines can be minimized. The line shape is called the Breit-Wigner line shape. Other effects that broaden spectral lines include the Doppler shift due to moving atoms in a gas, and collisions between atoms. The Doppler shift causes a Gaussian (not Lorentzian) broadening of the spectral lines. The width \( \Gamma \) of the spectral line due to the finite life time of the state is called the natural line width.
Now we use some of the things learned in the analysis of
natural line width to study other problems. We begin with the divergences
in the K-H formula. For simplicity consider elastic scattering, where
A + γ → A + γ', A = ground state. The cross section is
\[
\frac{d\sigma}{d\Omega'} = r^2 M^2
\]
where
\[
M = \varepsilon \varepsilon^* + \sum_{I+\lambda} \left( \frac{\langle A|\mathcal{E}^\lambda|I\rangle\langle I|\mathcal{E}|A\rangle}{\omega - \omega_{I\lambda}} - \frac{\langle A|\mathcal{E}^\lambda|I\rangle\langle I|\mathcal{E}^\lambda|A\rangle}{\omega + \omega_{I\lambda}} \right)
\]
(see p.3, 2/24/06). This term I is resonant when \( \omega \) (freq. of incident photon) = \( \omega_{I\lambda} \) (resonant freq. connecting ground state A with some excited state I).

The resonant denom is
\[
\omega - \omega_{I\lambda} = \omega - E_I + \epsilon_A \quad \text{(x=1 here)}.
\]
It comes out of the Dyson series by doing a time integral over
\[
e^{-i(\omega - E_I + \epsilon_A)t} = e^{-i(E_I - \epsilon_A - \omega)t}.
\]
The phase factor \( e^{-iE_I t} \) is the time evolution of the state I computed by
the unpert. Ham. \( H_0 \). The Dyson series is one of successive approximations,
in which we insert one approximation for the \( t \)-evolution (in this case,
the unpert. evol.) into a \( t \)-integral to get the next approximation.

However, we know that the actual time evolution of the unturned
state I is more closely given by
\[
e^{-i(E_I + \Delta E_I + \Delta E_x(\gamma) - i \gamma/2)t} = \text{(cont'd)}
\]
\[ e^{-i \tilde{E}_I t - \Gamma t/2} \]

where
\[ \tilde{E}_I = E_I + \Delta E_I^{(1)} + \Delta E_I^{(2)} \]
is the real part of the energy, corrected to 2nd order by interactions with
the field. See p. 8, 4/5/06 for the energy corrections, in a general
notation. Thus, in using this more accurate \( \tau \)-evolution for the
state \( I \) in the \( \tau \)-integral, we get a modified denominator
in the K-H formula:

\[ \omega - \tilde{E}_I + E_A + i \Gamma/2. \]

The energy of state \( A \) (\( E_A \)) should also be modified by \( \Delta E_A^{(1)} \) and
\( \Delta E_A^{(2)} \), but being the ground state it has an \( \infty \) life time and so
\( \Gamma_A = 0 \). Thus, we should really use \( \omega - \tilde{E}_I + E_A + i \Gamma/2 \), where
\( \Gamma \) refers to state \( I \). Let's henceforth interpret \( a_{IA} \) as \( \tilde{E}_I - \tilde{E}_A \).
Then the K-H denominator is \( \omega - \omega_{IA} + i \Gamma/2 \), and it no longer
vanishes when \( \omega = \omega_{IA} \).

When \( \omega \approx \omega_{IA} \), one term dominates in the K-H formula,

\[ M = \frac{\langle A | \bar{\Psi}_I \bar{\Psi}_I^* | I \rangle \langle I | \bar{\Psi}_A \bar{\Psi}_A^* | A \rangle}{\omega - \omega_{IA} + i \Gamma/2}, \]

\[ \frac{d\sigma}{d\Omega'} = \alpha^4 \alpha_0^2 \frac{|\langle A | \bar{\Psi}_I \bar{\Psi}_I^* | I \rangle|^2 |\langle I | \bar{\Psi}_A \bar{\Psi}_A^* | A \rangle|^2}{(\omega - \omega_{IA})^2 + \Gamma^2/4}. \]
To sketch the cross-section as a fun. of incident photon \( \omega \) we have something like (not to scale):

\[
\frac{d\sigma}{d\omega'}
\]

Near \( \omega = \omega_{IA} \) the one term expression (prev. page) gives the same Lorentzian dependence on \( \omega \) as we had for the natural line width. The FWHM is \( \Gamma/4 \) (in freq. units), which for E1 transitions at optical frequencies is \( \sim O(\alpha^3) \) in a.u. So if the freq. range in the plot above is \( O(1) \) in a.u. (typical optical freq's) then the width of the resonance is \( \sim 10^{-6} \). For \( \omega \) not near a resonance the K-H denominators are all \( O(1) \) in a.u., so \( \frac{d\sigma}{d\omega'} \sim \alpha^4 \alpha_0^2 \), pretty small by atomic standards. But on resonance \( (\omega = \omega_{IA}) \) the denominator is \( \sim \Gamma^2 \sim \alpha^6 \sim 10^{-13} \), so the height of the peak is \( \sim 10^{13} \times \) higher than the nonresonant values. This becomes over \( 10^{20} \) for M1 transitions. The total area under the resonant peak (width \( \sim \Gamma \), height \( \sim \Gamma \)) is order \( 1/\Gamma \), so in broad band radiation by far most of the scattering is
resonant, at least until the beam is depleted in the resonant frequency range. This is the explanation for the dark Fraunhofer lines in the solar spectrum (resonant scattering by cooler gases in the sun's atmosphere of the radiation coming from the photosphere).

Next we examine the real parts of the energy shift \( \Delta E_i^{(1)} \) and \( \Delta E_i^{(2)} \) due to the interaction of atomic electrons with the EM field. In general notation we have

\[
\Delta E_i^{(1)} = \langle i | V_i | i \rangle ,
\]

and

\[
\Delta E_i^{(2)} = \sum_{k \neq i} \left( \frac{P}{E_i - E_k} \right) |\langle k | V_i | i \rangle|^2 .
\]

We are not talking about the interaction of atomic electrons with real photons — that would be photon scattering, described by the K-H formula. Instead, we take the case that the photon state is the vacuum. Nevertheless, even in the vacuum there are fluctuations of the EM field, and the effects we shall find can be ascribed to the interaction of the electrons with those fluctuations.

The imaginary part \( \Gamma \) of the 2nd order energy shift is the decay rate \( (\nu = \Gamma/k) \) of an excited state \( B \), but what about the real energy shifts? To calculate these we must switch from the general notation above to notation specific
to the atom.

For the initial state \( |i\rangle \), write

\[
|i\rangle \rightarrow |B\rangle |0\rangle = |B0\rangle
\]

\( E_i \rightarrow E_B. \)

For the perturbing Hamiltonian, write

\( V \rightarrow H_1 + H_2 \)

where

\[
H_1 = \frac{e}{mc} \mathbf{p} \cdot \mathbf{A}(\vec{r})
\]

\[
H_2 = \frac{e^2}{2am^2c^2} \mathbf{A}(\vec{r})^2
\]

It's better to use ordinary units in this calculation. Then at 1st order we have

\[
\Delta E_B^{(1)} = \langle B0 | H_1 | B0 \rangle.
\]

But since \( H_1 \cdot \mathbf{A}(\vec{r}) \) can only create or destroy one photon, and since it is sandwiched between states with equal numbers of photons (namely, \( 0 \)), the result is \( 0 \). We must go to 2nd order to get an energy shift.

At 2nd order we have a sum on intermediate states \( \bar{k} \) (in general notation), which in principle is a sum over a complete set of states for the matter and field. But since \( |i\rangle \rightarrow |B0\rangle \) has no photons and since \( H_1 \) can only create or destroy one photon, the only intermediate states \( \bar{k} \) that are reachable from \( |B0\rangle \) are those with precisely one
As we identify

\[ |k\rangle \rightarrow |i\rangle \overline{a}_{\lambda}^{\dagger} |0\rangle \equiv |i\lambda\rangle \]

\[ E_k \rightarrow E_i + \hbar \omega \]

where \( i \) is an intermediate atomic state and \( \omega = \omega_k \). Then the energy shift at 2nd order and associated diagrams are

\[ \Delta E_B^{(2)} = \langle B_0 | H_1 | i\lambda \rangle \langle i\lambda | H_1 | B_0 \rangle + \sum_{i\lambda} \frac{\langle B_0 | H_1 | i\lambda \rangle \langle i\lambda | H_1 | B_0 \rangle}{E_B - E_i - \hbar \omega} \]

where the principal value is understood in the 2nd term.

The diagrams are the same as in the scattering of a photon (K-H formula), except the external photon lines are joined to form an internal loop.

The first diagram (from \( H_3 \)) does not contribute to the effect we wish to calculate, so we will ignore it. The reason will be left as an exercise. The second diagram can be made more explicit by substituting \( H_i = \frac{e}{mc} \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) \), then using the Fourier series for \( \mathbf{A}(\mathbf{r}) \),
\[ \mathcal{A}(\mathbf{r}) = \sqrt{\frac{2\pi \hbar c^2}{V}} \sum_{\lambda} \frac{1}{\sqrt{\omega}} \left[ a_{\lambda} \hat{e}_\lambda e^{i\mathbf{p}\cdot \mathbf{r}} + a^*_{\lambda} \hat{e}^*_\lambda e^{-i\mathbf{p}\cdot \mathbf{r}} \right], \]

and then carrying out the field part of the matrix element. This gives

\[ \Delta E_B^{(2)} = \left( \frac{e}{mc} \right)^2 \frac{2\pi \hbar c^2}{V} \sum_{\mathbf{k}} \sum_{\mathbf{p}} \sum_{\mu} \frac{1}{\omega} \left| \left< \mathbf{r} | \hat{p} \hat{e}^*_\mu e^{-i\mathbf{p}\cdot \mathbf{r}} | \mathbf{B} \right> \right|^2 \frac{E_B - E_{\mathbf{k}} - \hbar \omega}{E_B - E_{\mathbf{p}} - \hbar \omega} . \]

First we make the electric dipole approximation, \( e^{-i\mathbf{p}\cdot \mathbf{r}} \approx 1 \), which is valid for optical photons but not for photons with energy too much above \( \Delta mc^2 \) (optical photons have energies \( \sim \Delta^2 mc^2 \)). This implies a cut off at high photon energies, which we will return to later.

We are using nonrelativistic QM, so our calculations are only valid for NR energies anyway.

With this approximation, the only part of the integrand that depends on the polarization \( \mu \) of the photon or the direction of \( \mathbf{k} \) is \( \hat{e}_\lambda \).

Define \( \mathbf{p}_{\lambda B} = \left< \mathbf{r} | \hat{p} \hat{e}^*_\mu | \mathbf{B} \right> \),

and take \( V \to \infty \) to

\[ \sum_{\mathbf{k}} \to \frac{V}{(2\pi)^3} \int_0^\infty \mathbf{p} d\mathbf{p} \int d\Omega_k. \]

Then

\[ \sum_{\mu} \int d\Omega_k \left| \hat{e}^*_\mu \cdot \mathbf{p}_{\lambda B} \right|^2 = \frac{8\pi}{3} \left| \mathbf{p}_{\lambda B} \right|^2, \]

and we have
\[ \Delta E^{(2)}_B = \frac{2}{3\pi} \frac{e^2}{m^2} \sum_k \left| \vec{p}_{Bk} \right|^2 \int_0^\infty \frac{k^2 dk}{\omega} \frac{1}{\epsilon_B - \epsilon_I - \hbar \omega}. \]

Change variable of integration to \( E = \hbar \omega \) (\( k = E/kc \)), and we get

\[ \Delta E^{(2)}_B = \frac{4}{3\pi} \frac{(e^2)}{(hc)} \frac{1}{m c^2} \frac{1}{2m} \sum_k \left| \vec{p}_{Bk} \right|^2 \int_0^\infty \frac{E dE}{E_B - \epsilon_I - E}. \]

The integral diverges because of the upper limit \( \infty \). It is a kind of ultraviolet catastrophe. Since we are using NR QM we might guess that relativistic effects would impose a cutoff on the upper limit of the integral, say \( E_{max} \sim m c^2 \), but then the integral diverges linearly in the cutoff and in the absence of any better guess for the cutoff we do not have a useful result.

This divergent integral is an example of the kind of infinities that plagued QED in its first 20 years of existence. They occur whenever QED is pushed beyond lowest order. The lowest order results agree very well with experiment (e.g., the life time of excited states), but cannot be corrected to higher order (with this primitive version of the theory).

Prior to WW II no one knew how to interpret the energy shift \( \Delta E^{(2)}_B \) above, but on the other hand there was no clear disagreement between