Time dependent perturbation theory comments PhL 3.9.09

I have now read on this subject first in Schiff and then in Saxon. If I had to prepare my own lecture on this little subject, how would it go?

1. Recasting the Schrodinger Equation. **1**
2. System of first order linear differential equations -- a digression. **3**
3. Perturbation Expansion **3**
4. Initial Conditions and First Order Coefficients **4**
5. Second Order Coefficients **5**
6. Perturbation H' at some single frequency ω **6**
7. Interpretation of the Resonance Situations **7**
8. Treatment of an absorption resonance situation **8**
9. A form for the delta function. **8**
10. Continue treatment of an absorption resonance situation: The Golden Rule **9**
11. Treatment of Stimulated Emission **11**
12. Photoejection of an electron from a gas molecule. **12**
13. Second order transition rates and two-photon processes **12**

1. Recasting the Schrodinger Equation.

I would start out with Schiff 35.3 showing coefficients $a_n(t)$. In this formula, we have symbols u_n and E_n which are the eigenfunctions and energies of some problem $H_0 u_n = E_n u_n$. If there were no perturbation H', then this formula with *constant* $a_n(t)$ would be nothing more than the most general solution of this problem's SE, $\psi(r,t)$. We know that if we add some small H'(t), then the u_n and E_n are no longer solutions of the SE, and our expansion with constant a_n cannot be correct. We think however that maybe if H' is very small, then $a_n(t)$ might change very slowly in time and in the limit that $\lambda \to 0$, $a_n(t) \to$ constants.

Be the above as it may, suppose we just start with the SE for our full perturbed system

$$(H_0 + \lambda H')\psi = i\hbar\partial_t\psi$$

and suppose we "attempt to represent" a general solution of the SE in this way

$$\psi(r,t) = \Sigma_n\, a_n(t)\, u_n(r) \exp(-iE_n t/\hbar) \qquad \text{where } H_0 u_n = E_n u_n \qquad u_n = \text{orthonormal}$$

If we plug in this representation, we get

$$\text{LHS} = (H_0 + \lambda H')\, \Sigma_n\, a_n(t)\, u_n(r) \exp(-iE_n t/\hbar) = \Sigma_n\, a_n(t)\, (E_n + \lambda H')\, u_n(r) \exp(-iE_n t/\hbar)$$

$$\text{RHS} = i\hbar\partial_t \Sigma_n a_n(t)\, u_n(r) \exp(-iE_n t/\hbar)$$

$$= \Sigma_n u_n(r)\, i\hbar\partial_t [a_n(t) \exp(-iE_n t/\hbar)]$$

$$= \Sigma_n u_n(r)\, i\hbar [\dot{a}_n(t) \exp(-iE_n t/\hbar) + a_n(t) (-iE_n/\hbar)\exp(-iE_n t/\hbar)]$$

$$= \Sigma_n u_n(r)\, i\hbar [\dot{a}_n(t) + a_n(t) (-iE_n/\hbar)] \exp(-iE_n t/\hbar)$$

$$= \Sigma_n u_n(r) [i\hbar\, \dot{a}_n(t) + E_n a_n(t)] \exp(-iE_n t/\hbar)$$

We can then write LHS-RHS = 0 to get

$$\Sigma_n \exp(-iE_n t/\hbar) [a_n(t) (E_n + \lambda H') - i\hbar\, \dot{a}_n(t) - E_n a_n(t)] u_n(r) = 0$$

but two of the four terms cancel and this becomes

$$\Sigma_n \exp(-iE_n t/\hbar) [a_n(t) \lambda H' - i\hbar\, \dot{a}_n(t)] u_n(r) = 0$$

At this point, we multiply by $u_k^*(r)$ and integrate over space to get

$$\Sigma_n \exp(-iE_n t/\hbar) \int d^3r\; u_k^*(r) [a_n(t) \lambda H' - i\hbar\, \dot{a}_n(t)]\; u_n(r) = 0$$

$$\Sigma_n \exp(-iE_n t/\hbar) [a_n(t) \lambda H'_{kn} - i\hbar\, \dot{a}_n(t)\, \delta_{k,n}] = 0$$

$$\Sigma_n \exp(-iE_n t/\hbar)\, a_n(t) \lambda H'_{kn} - i\hbar\, \dot{a}_k(t) \exp(-iE_k t/\hbar) = 0$$

$$i\hbar\, \dot{a}_k(t) = \Sigma_n \exp(-i[E_n - E_k]t/\hbar) \lambda H'_{kn}(t)\, a_n(t) \qquad (*)$$

where we have defined matrix element H'_{kn} in the obvious manner.

If we can find a set of coefficients $a_k(t)$ which solve equations (*), then our trial $\psi(r,t)$ is in fact a solution of the new SE including $\lambda H'$. So yes, we can regard (*) as a restatement of the SE.

The big question is this: WHY is this a useful way to restate the SE? One answer is this: we can see that if H'=0, all the a_k must be constants, which is consistent with our starting position. And if λ is small, the a_n change *slowly*, another one of our starting ideas. Both these ideas are now explicit in (*). These ideas are consistent with the fact that we have "gone to the interaction picture", but let's not dwell on that concept here.

Equation (*) says that the time rate of change of an $a_k(t)$ coefficient (amplitude) depends on the size of all the other amplitudes, and on the size of the matrix elements shown and on the unperturbed state energy differences. This is a system of coupled first order differential equations with non-constant coefficients,

$$i\hbar\, da_k(t)/dt \; - \Sigma_n \{\exp(-i[E_n - E_k]t/\hbar)\, \lambda H'_{kn}(t)\}\; a_n(t) = 0$$

which we could rewrite generically as

$$i\hbar\, da_k(t)/dt \; + \Sigma_n\, h_{kn}(t)\, a_n(t) = 0 \qquad\qquad h_{kn}(t) = -\exp(-i[E_n - E_k]t/\hbar)\, \lambda H'_{kn}(t)$$

where $h_{kn}(t)$ are those non-constant coefficients.

2. System of first order linear differential equations -- a digression.

What do we know about solving such a system of equations? Since $H'_{kn}(t)$ can be an arbitrary function of t, we don't really have a closed form solution. Suppose instead of this system, we just had a single first order ODE which said

$$da(t)/dt = h(t)\, a(t)$$

We would solve this simpler "system" by rewriting it as

$$da(t)/a(t) = h(t)dt$$

$$\ln[\, a(t)\,] = \int_0^t h(t')dt'$$

$$a(t) = \exp\left[\int_0^t h(t')dt'\right]$$

which reminds us of the WKB but in time instead of space. But clearly this solution method does not work if we have a system of equations. Suppose we had a NxN system:

$$da_i(t)/dt = h(t)_{ij}\, a_j(t)$$

One can apply matrix techniques to express

$$d/dt\, \mathbf{a} = h\, \mathbf{a} \qquad\qquad h = \text{matrix} \qquad \mathbf{a} = \text{vector}$$

But no amount of fiddling around is going to produce anything other than a possible *formal* solution in terms of obscure operators. We can recast as a first order linear integral equation, but that does not solve the problem either.

3. Perturbation Expansion

So having paid passing due diligence to the general notion of a system of coupled first order ODE's, let's go back to our system of equations stated as (*) above

$$i\hbar\, \dot{a}_k(t) = \Sigma_n \exp(-i[E_n - E_k]t/\hbar)\, \lambda H'_{kn}(t)\, a_n(t) \qquad\qquad (*)$$

We admit that this system is too hard to "solve in general". BUT, we want to take advantage of the fact that the smallness parameter λ is sitting in there on the RHS, so we try to find a solution for $a_k(t)$ which is a power series in λ,

$$a_k(t) = a_k^{(0)}(t) + \lambda\, a_k^{(1)}(t) + \lambda^2\, a_k^{(2)}(t) + \ldots. = \Sigma_{s=0}\, a_k^{(s)} \lambda^s$$

Install this series into both sides of (*) to get

$$i\hbar\, \dot{a}_k(t) = \Sigma_n \exp(-i[E_n - E_k]t/\hbar)\, \lambda H'_{kn}(t)\, a_n(t) \qquad (*)$$

$$\Sigma_{s=0}\, i\hbar\, \dot{a}_k^{(s)} \lambda^s = \Sigma_n \exp(-i[E_n - E_k]t/\hbar)\, \lambda H'_{kn}(t)\, \Sigma_{s=0}\, a_n^{(s)} \lambda^s$$

$$= \Sigma_n \exp(-i[E_n - E_k]t/\hbar)\, H'_{kn}(t)\, \Sigma_{s=0}\, a_n^{(s)} \lambda^{s+1}$$

Let s' = s+1 on the RHS, to get

$$\Sigma_{s=0}\, i\hbar\, \dot{a}_k^{(s)} \lambda^s = \Sigma_n \exp(-i[E_n - E_k]t/\hbar)\, H'_{kn}(t)\, \Sigma_{s'=1}\, a_n^{(s'-1)} \lambda^{s'}$$

Break out the λ^0 term on the left, rename s' to s on the right

$$i\hbar\, \dot{a}_k^{(0)}(t) + \Sigma_{s=1}\, i\hbar\, \dot{a}_k^{(s)}(t) \lambda^s = \Sigma_n \exp(-i[E_n - E_k]t/\hbar)\, H'_{kn}(t)\, \Sigma_{s=1}\, a_n^{(s-1)}(t) \lambda^s$$

Now match powers of λ to get

$$\dot{a}_k^{(0)}(t) = 0 \qquad // \lambda^0 \text{ power}$$

$$\dot{a}_k^{(s)}(t) = (i\hbar)^{-1}\, \Sigma_n \exp(-i[E_n - E_k]t/\hbar)\, H'_{kn}(t)\, a_n^{(s-1)}(t) \qquad s > 0$$

It is convenient to integrate these equations from time t = 0 to time t = t:

$$a_k^{(0)}(t) = a_k^{(0)}(0)$$

$$a_k^{(s)}(t) = a_k^{(s)}(0) + (i\hbar)^{-1} \int_0^t dt'\, \Sigma_n \exp(-i[E_n - E_k]t'/\hbar)\, H'_{kn}(t')\, a_n^{(s-1)}(t') \qquad s > 0$$

4. Initial Conditions and First Order Coefficients

As our "initial conditions", let us suppose at t = 0 the system is 100% in some state "m" = u_m, so we have

$$a_n(0) = \delta_{n,m}$$

At t = 0 we also instantaneously turn on λ from value λ=0 to λ=λ, a step function. How shall we express this set of initial conditions in terms of our expansion for the a_n in powers of λ? Let's try this:

$$a_n^{(0)}(0) = \delta_{n,m} \qquad \text{and} \qquad a_n^{(s)}(0) = 0 \quad \text{for } s > 0$$

This says that no "correction terms" are activated at t=0. We then rewrite the above equation pair as:

$$a_k^{(0)}(t) = \delta_{k,m}$$

$$a_k^{(s)}(t) = (i\hbar)^{-1} \int_0^t dt' \, \Sigma_n \exp(-i[E_n - E_k]t'/\hbar) \, H'_{kn}(t') \, a_n^{(s-1)}(t') \qquad s > 0$$

The second equation for s=1 can then be written as (making use of the first equation along the way)

$$a_k^{(1)}(t) = (i\hbar)^{-1} \int_0^t dt' \, \Sigma_n \exp(-i[E_n - E_k]t'/\hbar) \, H'_{kn}(t) \, a_n^{(0)}(t')$$

$$= (i\hbar)^{-1} \int_0^t dt' \, \Sigma_n \exp(-i[E_n - E_k]t'/\hbar) \, H'_{kn}(t') \, \delta_{n,m}$$

$$= (i\hbar)^{-1} \int_0^t dt' \exp(-i[E_m - E_k]t'/\hbar) \, H'_{km}(t')$$

$$= (i\hbar)^{-1} \int_0^t dt' \exp(-i\omega_{mk}t') \, H'_{km}(t') \qquad \text{where} \quad \hbar\omega_{mk} = E_m - E_k$$

This is a very clean and well-defined result, something we can make use of. As a passing observation, we can note that if H' varies slowly with time (slowly relative to ω_{mk}) and if t is long relative to ω_{mk} , the phasor dices up the integrand into cancelling fragments, the integral is small, and nothing very interesting happens. Unless state k is actually the starting state m or some state degenerate with m or very close to m in energy, the amplitude $a_k^{(1)}(t)$ for slowly varying and small H' is small for all t > 0.

5. Second Order Coefficients

Just while we are here, let's install our result for $a_k^{(1)}(t)$ into the s=2 equation just to see what things look like in second order:

$$a_k^{(2)}(t) = (i\hbar)^{-1} \int_0^t dt' \, \Sigma_n \exp(-i[E_n - E_k]t'/\hbar) \, H'_{kn}(t') \, a_n^{(1)}(t')$$

$$= (i\hbar)^{-1} \int_0^t dt' \, \Sigma_n \exp(-i\omega_{nk}t') \, H'_{kn}(t') \, \{ \; (i\hbar)^{-1} \int_0^{t'} dt'' \exp(-i\omega_{mn}t'') \, H'_{nm}(t'') \, \}$$

$$= (i\hbar)^{-2} \, \Sigma_n \int_0^t dt' \exp(-i\omega_{nk}t') \, H'_{kn}(t') \int_0^{t'} dt'' \exp(-i\omega_{mn}t'') \, H'_{nm}(t'')$$

We can see that if we keep doing this for each higher order, we build up quite a mess, and a graphical method certainly is suggested.

6. Perturbation H' at some single frequency ω

Either to see the system's response to perturbation at frequency ω, or as the first step in a Fourier analysis of the system response to an arbitrary time function, let's assume now that we have

$$H'_{ij}(t) = 2H'_{ij} \sin(\omega t)$$

where we use a real function sin(ωt) so we can think of this H' as perhaps caused by a real electric field or some such thing. The factor of two is included in the definition of H'_{ij} so that our result comes out in a traditional historical form known as Fermi's Golden Rule.

Our first integral of interest is then

$$a_k^{(1)}(t) = (i\hbar)^{-1} \int_0^t dt' \exp(-i\omega_{mk}t') H'_{km}(t') = (i\hbar)^{-1} 2H'_{km} \int_0^t dt' \exp(-i\omega_{mk}t') \sin(\omega t)$$

$$= (i\hbar)^{-1} 2H'_{km} (2i)^{-1} \int_0^t dt' \exp(-i\omega_{mk}t') [e^{i\omega t} - e^{-i\omega t}]$$

$$= [(i\hbar)^{-1} 2H'_{km} (2i)^{-1} \int_0^t dt' [\exp(-i(\omega_{mk}-\omega)t')] - (\omega \rightarrow -\omega)$$

$$= (i\hbar)^{-1} 2H'_{km} (2i)^{-1} [-i (\omega_{mk}-\omega)]^{-1} [\exp(-i(\omega_{mk}-\omega)t')]_0^t - (\omega \rightarrow -\omega)$$

$$= (i\hbar)^{-1} 2H'_{km} (2i)^{-1} [-i (\omega_{mk}-\omega)]^{-1} [(\exp(-i(\omega_{mk}-\omega)t - 1)] - (\omega \rightarrow -\omega)$$

$$= (\hbar)^{-1} 2H'_{km} (2i)^{-1} [(\omega_{mk}-\omega)]^{-1} [(\exp(-i(\omega_{mk}-\omega)t - 1)] - (\omega \rightarrow -\omega)$$

$$= H'_{km} (i\hbar)^{-1}(\exp(-i(\omega_{mk}-\omega)t - 1)/ (\omega_{mk}-\omega) - (\omega \rightarrow -\omega)$$

$$= H'_{km} (i\hbar)^{-1}(\exp(-i(-\omega_{km}-\omega)t - 1)/ (-\omega_{km}-\omega) - (\omega \rightarrow -\omega)$$

$$= - H'_{km} (i\hbar)^{-1}(\exp(i(\omega_{km}+\omega)t - 1)/ (\omega_{km}+\omega) - (\omega \rightarrow -\omega)$$

$$= [- H'_{km} (i\hbar)^{-1}(\exp(i(\omega_{km}+\omega)t - 1)/ (\omega_{km}+\omega)] - (\omega \rightarrow -\omega)$$

$$= [- H'_{km} (i\hbar)^{-1}(\exp(i(\omega_{km}+\omega)t - 1)/ (\omega_{km}+\omega)] - [- H'_{km} (i\hbar)^{-1}(\exp(i(\omega_{km}-\omega)t - 1)/ (\omega_{km}-\omega)]$$

$$= - H'_{km}/(i\hbar) \{ (\exp(i(\omega_{km}+\omega)t - 1)/ (\omega_{km}+\omega) - (\exp(i(\omega_{km}-\omega)t - 1)/ (\omega_{km}-\omega) \}$$

which by the way agrees with Schiff page 283 (35.11). We can see that there are going to be resonance situations when $\omega = \pm \omega_{km}$. If we stay far from such resonances, we may conclude by staring at the above that $a_k^{(1)}(t)$ starts small and remains small for all time t, providing H'_{km} is small, specifically, provided

$$|H'_{km}| << \hbar(\omega_{km} \pm \omega)$$

where now λ is included in H'. In other words, our system starts in state "m" and basically stays there, with the amplitude of being off in state "k" being some tiny oscillatory amount that comes and goes.

7. Interpretation of the Resonance Situations

On the other hand, if we have $\omega \approx \pm \omega_{km}$, which means $E_k - E_m = \mp \hbar\omega$, the amplitude $a_k^{(1)}(t)$ is no longer going to be small, and $a_k^{(1)}(t)$ is going to be significant, as we shall see in the next section. If $E_k > E_m$, we are going to interpret the case $E_k - E_m = + \hbar\omega$ ($\omega>0$) as our system absorbing a "photon" (or some generic particle carrying energy quantum $\hbar\omega$) and being moved *up* in energy from state m to state k, and this change in state amplitudes is in fact caused by this "photon" or its "field" , which is what is making the perturbation H'. In the case where H' does in fact represent an electromagnetic field of some sort, we are right here showing that atomic spectral absorption of light is falling out in our hands from just the Schrodinger Equation and our dutiful application of time dependent perturbation theory to this system, where we assume the interaction with light is a "weak" interaction. The situation with the other "sign" , which is to say $E_k - E_m = - \hbar\omega$ ($\omega>0$), means we have $E_m - E_k = \hbar\omega$ and our "atom" or whatever system we have has then *emitted* a photon and gone down to the lower energy $E_k < E_m$. Since we are treating the field classically (but our atom quantum mechanically), the field -- although weak -- still has zillions of quanta and we don't notice in the quantity H' that the field has changed by ± 1 photon. Our focus here is on the atom, not the field, and we are seeing that the field has two resonance situations with respect to final energy level E_k and initial energy level E_m. One situation we interpret as the atom being stimulated by the field to absorb one quantum $\hbar\omega$ from the field and go to a state of increased energy, and the other situation we interpret as the atom being stimulated to emit one quantum $\hbar\omega$ into the field and to drop down to a state of reduced energy. This latter phenomenon is involved in causing a laser to "lase" after it has been pumped to an energy inverted state, "stimulated emission". Of course these things only happen if the system is in the right state "m" such that another (unoccupied) state "k" is the right distance away in energy to match $\hbar\omega$. Otherwise we don't achieve the resonance situation and amplitude $a_k^{(1)}(t)$ remains small.

As we continue in this theory development, we would like to see, for photon absorption, that our final state amplitude $|a_k^{(1)}(t)|$ grows in time, while our initial state amplitude $|a_m^{(1)}(t)|$ decreases in time. Our interpretation would then be then more justified. If we were to leave the perturbation "on" for a long time, we might even see $a_k = 1$ and $a_m = 0$ after a while, and then stimulated emission would dominate, and we would then see a_k decrease and a_m increase again. The population of these two states would then oscillate back and forth as long as the perturbing field is applied. Here we are assuming that our two states m and k are perhaps the ground state and some excited state of an atom, so that the atomic electron is shuttling up and down between these two states over time, as stimulated absorption and emission of energy from the field occurs. In the usual Golden Rule development which we shall do soon, the state "k" is usually assumed to be some high energy plane wave state where an electron has been completely ejected from the atom by the absorption of the incoming photon. In this case, that ejected electron tends to wander "far

away" in the "box" and the reverse process of simulated emission is less likely to occur. That ejected electron has to find the "hole" in the atom that emitted it and fall back into that hole. These plane wave states "k" are, in the limit of a large "box", continuum energy states, whereas we have just been discussing "k" as a discrete energy excited state or ground state of an atom.

8. Treatment of an absorption resonance situation.

The situation here is $\hbar\omega = E_k - E_m > 0$ so $E_k > E_m$ and the "atom" moves up from state E_m to state E_k, where maybe E_m is the atom's ground state. So we are talking $\omega = \omega_{km}$ or at least $\omega \approx \omega_{km}$. In our expression above for $a_k^{(1)}(t)$ we throw out the first term which is then small, and say,

$$a_k^{(1)}(t) \approx H'_{km}/(i\hbar) \{ (\exp(i(\omega_{km} - \omega)t - 1)/(\omega_{km} - \omega) \} = A (e^{ist} - 1)/s$$

where $s = \omega_{km} - \omega$. This is the "amplitude" $a_k^{(1)}(t)$ and we square to get the probability of being in state "k",

$$|a_k^{(1)}(t)|^2 = |A|^2/s^2 * (e^{ist} - 1)(e^{-ist} - 1) = |A|^2/s^2 * (1 - e^{-ist} - e^{ist} + 1)$$

$$= |A|^2/s^2 * (2 - [e^{ist} + e^{-ist}]) = |A|^2/s^2 * (2 - 2\cos(st))$$

$$= 2 |A|^2/s^2 (1 - \cos(st)) = 4 |A|^2/s^2 * \sin^2(st/2)$$

We want to show that as $s = \omega_{km} - \omega \rightarrow 0$, this expression becomes a delta function of some sort, so we have another small digression.

9. A form for the delta function.

The mathematical result we wish to use is this:

$$\lim_{a \to 0} [(a/\pi x^2) \sin^2(x/a)] = \delta(x)$$

How would we prove this math result before using it? We just need to show that in the limit of interest, here meaning $a \rightarrow 0$, we have a sequence of functions $f_a(x) = (a/\pi x^2) \sin^2(x/a)$ which approaches in the limit a nice symmetric peaked thing at x=0 which has unit area. Let's write

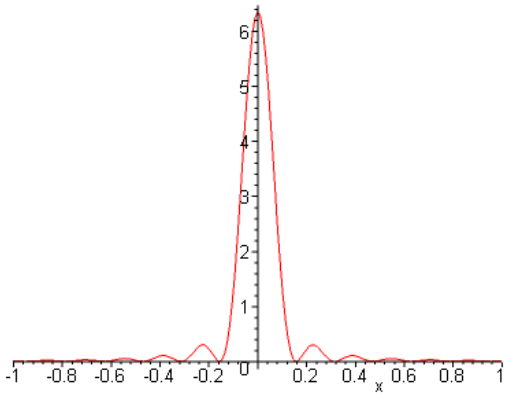
$$f_a(x) = (a/\pi x^2) \sin^2(x/a) = a * \sin^2(x/a) / [\pi x^2] = a^{-2} * a * \sin^2(x/a) / [\pi x^2 a^{-2}]$$

$$= (1/\pi a) \sin^2(x/a) / (x/a)^2 = (1/\pi a) [\sin(y)/y]^2 \qquad y = x/a$$

In this form we can see that for a given a, we have $f_a(0) = (1/\pi a)$, so the central height of our delta function candidate is increasing as $a \rightarrow 0$. At the same time, the "width" is shrinking. If we approximate this width as the distance from x=0 to the first zero of sin(y), we get $x/a = \pi$ so width = πa. As a becomes small, the only significant contribution to the area under $f_a(x)$ comes from the central peak which has height $f_a(0) = (1/\pi a)$ and width πa and so has area 1. This is of course just a lucky result, and we need to

show that the area really is exactly 1 in order to confirm that the limit of the sequence $f_a(x)$ really is the delta function $\delta(x)$. It is useful just to see the shape of this squared "sinc" function for some small value of a in order to see the point which is then fairly obvious,

```
a := .05:
plot((1/(Pi*a))*(sin(x/a)/(x/a))^2,x=-1..1);
```



The function $f_a(x)$ is symmetric about x=0, and it is clear that in the limit $a \to 0$ it is going to act as a delta function provided the area under it is unity, so that is the only thing we now have to show. But for any value of a including the limit we have, using x = ay,

$$\int_{-\infty}^{\infty} dx\ (1/\pi a)\ [\sin(y)/y]^2 \ = \ \int_{-\infty}^{\infty} dy\ (1/\pi)\ [\sin(y)/y]^2$$

$$= (2/\pi)\ \int_{0}^{\infty} dy\ \sin^2(y)/y^2 = (2/\pi) * \pi/2\ = 1 \qquad \text{// a standard definite integral, look it up.}$$

This we have shown that

$$\lim_{a \to 0} [\ (a/\pi x^2)\ \sin^2(x/a)]\ = \delta(x)$$

which we can rewrite in the form we will actually use as

$$\lim_{b \to \infty} [\ \sin^2(bx)/(b\pi x^2)]\ = \delta(x)$$

where we have just taken b = 1/a.

10. Continue treatment of an absorption resonance situation: The Golden Rule

We had

$$|\ a_k^{(1)}(t)|^2 \ = \ 4\ |A|^2\ /s^2 * \sin^2(st/2) \qquad s = (\omega_{km} - \omega) \qquad A = H'_{km}/(i\hbar)$$

and we have the mathematical fact that

$$\lim_{b\to\infty} [\sin^2(bx)/(b\pi x^2)] = \delta(x)$$

We take

$$b = t \qquad x = s/2 \qquad \text{so} \qquad bx = st/2$$

It is the duration of our applied perturbation t that we are going to take "large" which we approximate by saying $t \to \infty$. So here is our mathematical fact

$$\lim_{t\to\infty} [\sin^2(ts/2)/(t\pi(s/2)^2)] = \delta(s/2)$$

Thus we need to "prepare" our probability properly so we can take this limit:

$$|a_k^{(1)}(t)|^2 = 4|A|^2/s^2 * \sin^2(st/2) = 4|A|^2 * \sin^2(ts/2) / [s^2]$$

$$= 2^{-2}\, t\, \pi\, 4|A|^2 * \sin^2(ts/2) / [s^2\, 2^{-2}\, t\, \pi]$$

$$= \pi |A|^2 t \{ \sin^2(ts/2) / (t\pi(s/2)^2) \}$$

But first we want to divide both sides by t to get

$$|a_k^{(1)}(t)|^2 / t = \pi |A|^2 \{ \sin^2(ts/2) / (t\pi(s/2)^2) \}$$

The LHS is the probability of being in state "k" after having the perturbation turned on for time duration t, divided by this amount of time t, so it is the *rate* at which the system is flowing from state "m" into state "k" measured in units of probability per second. We might call this the transition rate. We can now take the limit $t\to\infty$ and we have

$$\lim_{t\to\infty} (|a_k^{(1)}(t)|^2 / t) = \pi |A|^2 \lim_{t\to\infty} \{ \sin^2(ts/2) / (t\pi(s/2)^2) \}$$

$$= \pi |A|^2 \delta(s/2) = 2\pi|A|^2 \delta(s) = (2\pi/\hbar^2) |H'_{km}|^2 \delta(\omega - \omega_{km})$$

= transition rate

It is traditional to define $E \equiv \hbar\omega$ so this becomes

$$\text{transition rate from "m" to "k"} = (2\pi/\hbar) |H'_{km}|^2 \delta(E - (E_k - E_m)) = (2\pi/\hbar) |H'_{km}|^2 \delta(E_k - (E_m + E))$$

where:

$H'_{km}(t) = 2H'_{km} \sin(\omega t)$ = the applied perturbation Hamiltonian

$E = \hbar\omega$

E_k, E_m = unperturbed eigenenergies of the states k and m

This then is a traditional form of Fermi's Golden Rule for the state-to-state transition rate in a QM system which is acted upon by a weak sinusoidal perturbation. In our absorption situation, the delta function enforces energy conservation and says that $E_k = E_m + \hbar\omega$. The "atomic" state transitions "up" in energy from state m up to state k by absorbing a photon of energy $\hbar\omega$ from the perturbing field, and energy is thus conserved.

In an atomic absorption experiment, the Golden Rule predicts the rate at which an atom will absorb photons of light and make transitions between two states linked by $\hbar\omega$. The light source in the experiment will have a frequency intensity spectrum $I(\omega)$ which includes our frequency of interest ω_{km}. The Golden rule then predicts

$$\text{atomic transitions per second per atom} = \int d\omega \; I(\omega) \, (2\pi/\hbar^2) \, |H'_{km}|^2 \, \delta(\omega - \omega_{km})$$

$$= (2\pi/\hbar^2) \, |H'_{km}|^2 \, I(\omega_k)$$

In such an experiment, state "m" would be the ground state of some gas atom like He, and "k" would be some excited state. One would measure the absorption rate indirectly by observing the corresponding decay rate from these excited states, since "what goes up must eventually come down". This experiment could of course also be done with "molecules" like H_2 instead of atoms, but then "m" and "k" are molecular eigenstates.

We might wonder "how large does t have to be?" for our delta function approximation to be valid. The answer is that t has to be lots of periods of the frequency $\omega \approx \omega_{km}$. This is not difficult to achieve in an experiment such as those described above. We know that for very *short* periods t such as one might arrange in a pulsed laser experiment, our "energy conservation" can be violated in the sense of the uncertainty principle which says $\Delta E \Delta t \geq \hbar$.

11. Treatment of Stimulated Emission

Here we just take "the other term" in our original expression for $a_k^{(1)}(t)$. In terms of absolute value, this is the same as the term we used for absorption, but we need to replace $\omega \rightarrow -\omega$. Then everything goes through exactly as in the case of absorption, but we make this change at each step. Here are some of those steps:

$$a_k^{(1)}(t) \approx -H'_{km}/(i\hbar) \; \{ \; (\exp(i(\omega_{km}+\omega)t - 1)/(\omega_{km}+\omega) \; \} = A \, (e^{ist} - 1)/s \quad s = (\omega_{km} + \omega)$$

$$|a_k^{(1)}(t)|^2 = 4 \, |A|^2 / s^2 * \sin^2(st/2) \qquad A = H'_{km}/(i\hbar)$$

$$\text{transition rate from "m" to "k"} = (2\pi/\hbar) \, |H'_{km}|^2 \, \delta(E + (E_k - E_m)) = (2\pi/\hbar) \, |H'_{km}|^2 \, \delta(E_k - (E_m - E))$$

where the last result is the Golden Rule for stimulated emission. Energy conservation now says that

$$E_k = E_m - \hbar\omega$$

so now we assume in terms of our experiments that E_m is an initially excited atomic state, and E_k is the ground state, and the atom now emits a photon $\hbar\omega$ as it drops in energy from E_m down to E_k. Since H' is Hermitian, we know that $| H'_{km} |^2 = | H'_{mk} |^2$, by the way. We may conclude that the rate of stimulated absorption from state m to state k is the same as the rate of stimulated emission from state k to m, per atom, assuming in the first case that an atom is initially in state m, and in the second case the atom is initially in state k.

12. Photoejection of an electron from a gas molecule.

We won't do this problem right now, but it is the one most books talk about after introducing the Golden Rule (eg, Schiff). The perturbing energy $\hbar\omega$ is now assumed large enough that an electron in some initial state "m" in an atom ends up knocked out completely from the atom and is then in a "free particle" state for the final state "k". The atom or molecule in question is then left as a positive ion, so this would be an photo-ionization process. It is straightforward to compute the density of states $\rho(E_k)$ for the final electron, and then the Golden rule gives this result for the ionization rate:

$$\text{transition rate from "m" to "k"} = \int dE_k\, \rho(E_k)(2\pi/\hbar) | H'_{km} |^2 \delta(E_k - (E_m + E))$$

$$= (2\pi/\hbar) | H'_{km} |^2 \rho(E_m + \hbar\omega)$$

Here E_m would the (negative) binding energy of the gas molecules. The matrix element H' would be computed using the atomic initial state "orbital" wavefunction for "m", and the plane wave state for "k".

13. Second order transition rates and two-photon processes

I have never attempted this (in modern history), but we can take a quick shot at it. First, here is the first order amplitude for absorption taken from above, now expressed as going from starting state "m" to state "n":

$$a_n^{(1)}(t) \approx A_{nm} (e^{ist} - 1)/s \qquad s = \omega_{nm} - \omega \qquad A_{nm} = H'_{nm}/(i\hbar)$$

and here is our formula for the second order amplitude,

$$a_k^{(2)}(t) = (i\hbar)^{-1} \int_0^t dt' \Sigma_n \exp(-i[E_n - E_k]t'/\hbar)\, H'_{kn}(t') \{ a_n^{(1)}(t') \}$$

$$= (i\hbar)^{-1} \int_0^t dt' \Sigma_n \exp(-i\omega_{nk}t')\, H'_{kn}(t')\, A_{nm} (e^{ist'} - 1)/s$$

But of course we know that, as used earlier,

$$H'_{kn}(t') = 2H'_{kn} \sin(\omega t')$$

so we get

$$a_k^{(2)}(t) = (i\hbar)^{-1} \int_0^t dt' \Sigma_n \exp(-i\omega_{nk}t') 2H'_{kn} \sin(\omega t') A_{nm} (e^{ist'} - 1)/s$$

$$= \Sigma_n A_{kn} A_{nm} \int_0^t dt' \exp(-i\omega_{nk}t') \sin(\omega t') (\exp(i(\omega_{nm} - \omega)t') - 1)/(\omega_{nm} - \omega)$$

$$= \Sigma_n A_{kn} A_{nm} /(\omega_{nm} - \omega) \int_0^t dt' \exp(-i\omega_{nk}t') \sin(\omega t') (\exp(i(\omega_{nm} - \omega)t') - 1)$$

The integral is of course doable and contains 4 terms and in the result we will see various kinds of resonance situations. Each of these will have a photon interpretation, but now there will be two photons. The first photon takes us from state "m" to intermediate state "n" (summed over in our formula) with amplitude A_{nm} . The second photon takes us from this intermediate state "n" to a final state "k" with amplitude A_{kn}. The resonance for this case will yield a delta function which expresses energy conservation for this combined two-photon process. Either photon could represent absorption or emission. There will be some transition rate and a corresponding Golden Rule. The rate will be much less than the first order perturbation theory transition rate because we now have a λ^2 process where $\lambda = 1/137$ so to speak. So it is possible for an atom to move from state "m" to state "k" by "simultaneously" absorbing two photons of possibly different energy such that $\hbar\omega_1 + \hbar\omega_2 = E_k - E_m$, but the rate is small. The atom might instead simultaneously absorb and emit a photon of the same energy, or emit two photons. Schiff has a few comments on this, and I am sure there is lots of literature available on the subject.