Time-dependent Hamiltonians and the rotating wave approximation

Consider a 2 state system with

$$\hat{H}_o |a\rangle = E_a |a\rangle$$
$$\hat{H}_o |b\rangle = E_b |b\rangle \qquad (1)$$

In addition to the system Hamiltonian $\hat{H}_o$ we also turn on a <u>time dependent</u> <u>perturbation</u> $\hat{V}(t)$. The total Hamiltonian is therefore

$$\hat{H}(t) = \hat{H}_o + \hat{V}(t) \qquad (2)$$

Our goal is to solve the time-dependent S-Eq

$$\boxed{i\hbar \frac{d|\alpha(t)\rangle}{dt} = \hat{H}(t)|\alpha(t)\rangle} \qquad (3)$$

Note that the solution $|\alpha(t)\rangle = e^{-i\hat{H}t/\hbar}|\alpha(0)\rangle$ is <u>not</u> valid in this case. It only holds for time independent Hamiltonians.

If we use $|a\rangle$ and $|b\rangle$ as a basis then we may write the general state of the system as

$$|\alpha(t)\rangle = c_a(t)|a\rangle + c_b(t)|b\rangle = \begin{bmatrix} c_a(t) \\ c_b(t) \end{bmatrix} \qquad (4)$$

We may also express $\hat{H}(t)$ in this basis. We have

$$\hat{H}_o = \begin{bmatrix} E_a & 0 \\ 0 & E_b \end{bmatrix}$$

nd

$$\hat{V}(t) = \begin{bmatrix} V_{aa}(t) & V_{ab}(t) \\ V_{ba}(t) & V_{bb}(t) \end{bmatrix}$$

It turns out that in almost all cases of interest

$$V_{aa} = V_{bb} = 0 \qquad (5)$$

oreover, since $V^{+}(t) = V(t)$ we must have $V_{ba} = V_{ab}^{*}$.
hus the total Hamiltonian in the $|a\rangle$, $|b\rangle$ basis becomes

$$\hat{H} = \begin{bmatrix} E_a & V_{ab}(t) \\ V_{ab}^{*}(t) & E_b \end{bmatrix} \qquad (6)$$

Hence, Eq (3) may be written as

$$\boxed{i\hbar \frac{d}{dt}\begin{bmatrix} c_a \\ c_b \end{bmatrix} = \begin{bmatrix} E_a & V_{ab}(t) \\ V_{ab}^{*}(t) & E_b \end{bmatrix}\begin{bmatrix} c_a \\ c_b \end{bmatrix}} \qquad (7)$$

or, explicitly

$$\boxed{\begin{aligned} i\hbar\, \dot{c}_a &= E_a c_a + V_{ab}(t)\, c_b \\ i\hbar\, \dot{c}_b &= V_{ab}^{*}(t)\, c_a + E_b c_b \end{aligned}} \qquad (8)$$

hese are the equations you need to solve in a time-dependent problem. Usually they are very complicated to be solved.

The interaction picture

There is a trick which makes the problem a little bit easier which is called the interaction picture. The idea is to define

$$c_a(t) = \gamma_a(t)\, e^{-iE_a t/\hbar}$$
$$c_b(t) = \gamma_b(t)\, e^{-iE_b t/\hbar} \qquad (9)$$

This makes sense because, if $V=0$, then these would be the solutions of Eq (8), with $\gamma_{a,b}$ a constant. We now have

$$i\hbar \dot{c}_a = i\hbar \dot{\gamma}_a e^{-iE_a t/\hbar} + E_a c_a$$

Hence, this term will cancel the first term on the right of Eq (8):

$$i\hbar \dot{\gamma}_a e^{-iE_a t/\hbar} = V_{ab}\, \gamma_b\, e^{-iE_b t/\hbar}$$
$$i\hbar \dot{\gamma}_b e^{-iE_b t/\hbar} = V_{ab}^{*}\, \gamma_a\, e^{-iE_a t/\hbar}$$

It is convenient to define

$$\boxed{\omega_0 = \frac{E_b - E_a}{\hbar}} \qquad (10)$$

which is the natural frequency of transition between the two states. We then finally arrive at

$$\boxed{\begin{aligned} i\hbar \dot{\gamma}_a &= V_{ab}(t)\, e^{-i\omega_0 t}\, \gamma_b \\ i\hbar \dot{\gamma}_b &= V_{a\hat{b}}(t)\, e^{i\omega_0}\, \gamma_a \end{aligned}} \qquad (11)$$

these equations are exact. Once we find the functions $\gamma_{a,b}(t)$ we then have the full state

$$|\alpha(t)\rangle = \gamma_a(t)\, e^{-iE_a t/\hbar} |a\rangle + \gamma_b(t)\, e^{-iE_b t/\hbar} |b\rangle \qquad (12)$$

We will usually be interested in the following problem. Suppose that at $t=0$ the system is with certainty in $|a\rangle$, that is

$$\gamma_a(0) = 1 \qquad \gamma_b(0) = 0 \qquad (13)$$

then, after a time t has ellapsed we ask what is the probability that a transition occurred from a to b. that is, we ask about

$$\boxed{P_t(a \to b) = |\langle b|\alpha(t)\rangle|^2 = |\gamma_b(t)|^2} \qquad (14)$$

If $\hat{V}=0$ this probability is zero because $|a\rangle$ would be a tationary state of $\hat{H} = \hat{H}_0$. But when $\hat{V} \neq 0$ this will not be zero.

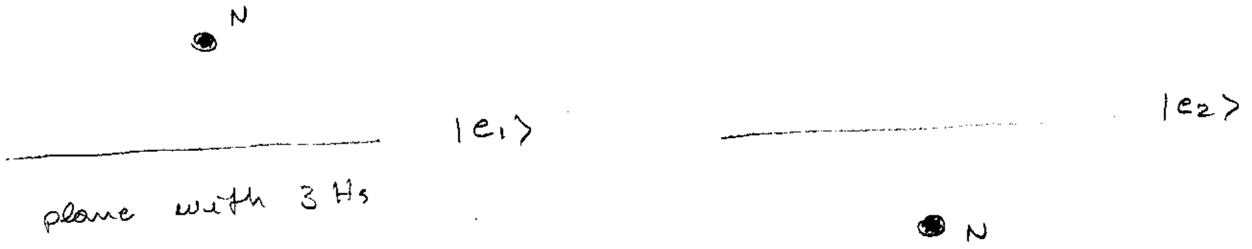
Finally, Eq (11) holds for any form of $V_{ab}(t)$. But we will mostly be interested with sinusoidal potentials

$$V_{ab}(t) = V_0 \cos \omega t \qquad (15)$$

here ω is the driving frequency, not to be confused with e natural frequency ω_0.

Example: the amonia molecule

The amonia molecule NH_3 has a tetragonal shape, with the 3 H atoms lying on a plane.



The N atom may be either up or down. If it is up we say the system is in a state $|e_1\rangle$. If it is down it is in a state $|e_2\rangle$.

The energy in either state is E_0. However, due to quantum mechanical tunneling, the N atom may cross through the plane of the 3 hydrogens and switch from one position to the other. Thus, the Hamiltonian of the system is, in the $|e_1\rangle, |e_2\rangle$ basis

$$\hat{H}_0 = \begin{bmatrix} E_0 & -A \\ -A & E_0 \end{bmatrix} \tag{16}$$

where A is the amplitude for the system to flip from one configuration to the other. (The minus sign is just for convenience). The eigenvalues and eigenvectors are

$$E_a = E_0 - A \qquad |a\rangle = \frac{|e_1\rangle + |e_2\rangle}{\sqrt{2}} \tag{17}$$

$$E_b = E_0 + A \qquad |b\rangle = \frac{|e_1\rangle - |e_2\rangle}{\sqrt{2}}$$

Thus, the transition frequency is

$$w_0 = \frac{E_b - E_a}{\hbar} = \frac{2A}{\hbar} \tag{18}$$

Experimentally we know that this frequency lies in the micro-wave region with

$$f_0 = \frac{w_0}{2\pi} \simeq 24 \text{ kHz}$$

The amania molecule has a permanent electric moment μ

If we turn on an electric field the energy of interaction will be $-\vec{\mu}\cdot\vec{\mathcal{E}} = \mu\mathcal{E}$ in the up state and $-\mu\mathcal{E}$ in the down state. Thus, in the presence of an electric field the total Hamiltonian will be

$$\hat{H} = \begin{bmatrix} E_0 + \mu\mathcal{E} & -A \\ -A & E_0 - \mu\mathcal{E} \end{bmatrix} = \hat{H}_0 + \hat{V}$$

But to apply Eq (11) we need $\hat{V}$ in the $|a\rangle, |b\rangle$ basis, not the $|e_1\rangle, |e_2\rangle$ basis. We have

$$V_{aa} = \langle a|\hat{V}|a\rangle = \frac{1}{2}\begin{bmatrix} 1 & 1 \end{bmatrix}\begin{bmatrix} \mu\mathcal{E} & 0 \\ 0 & -\mu\mathcal{E} \end{bmatrix}\begin{bmatrix} 1 \\ 1 \end{bmatrix} = 0$$

and similarly $V_{bb} = 0$. As I said, this is very common. Finally we have

$$V_{ab} = \langle a|V|b\rangle = \frac{\mu\mathcal{E}}{2}\begin{bmatrix} 1 & 1 \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 1 \\ -1 \end{bmatrix} = \mu\mathcal{E}$$

Thus, the term V_{ab} in Eq (11) will, in this case, be simply

$$\boxed{V_{ab}(t) = \mu\mathcal{E}(t)} \qquad (19)$$

The rotating wave approximation

Let us go back to Eq (11) and assume a sinusoidal perturbation, as in Eq (15). We then have

$$i\hbar\dot{\psi}_a = \frac{V_0}{2}\left(e^{i\omega t} + e^{-i\omega t}\right)e^{-i\omega_0 t}\psi_b$$
$$i\hbar\dot{\psi}_b = \frac{V_0}{2}\left(e^{i\omega t} + e^{-i\omega t}\right)e^{i\omega_0 t}\psi_a$$

Letting

$$\lambda = \frac{V_0}{\hbar} \tag{20}$$

we get

$$\boxed{\begin{aligned} i\dot{\psi}_a &= \frac{\lambda}{2}\left[e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}\right]\psi_b \\ i\dot{\psi}_b &= \frac{\lambda}{2}\left[e^{i(\omega+\omega_0)t} + e^{-i(\omega-\omega_0)t}\right]\psi_a \end{aligned}} \tag{21}$$

These equations are <u>exact</u>. Unfortunately they cannot be solved exactly in terms of elementary functions. They can be solved, however, under a certain approximation first discovered by Rabi. The idea is that in most cases we want the driving frequency ω to be close to the natural frequency ω_0. This is the situation of <u>resonance</u>. In Eq (21) we see two terms, one oscillating with frequency $\omega+\omega_0$ and the other with frequency $\omega-\omega_0$. If $\omega\sim\omega_0$ the former will correspond to very fast oscillations which average to zero. Thus, the idea is to neglect the terms which oscillate with $\omega+\omega_0$. This will be good provided $\omega\sim\omega_0$ and also if ε is small. Otherwise, strong non-linear effects would come into play.

This idea is called the rotating wave approximation and it is very commonly used in physics. We therefore simplify Eq (21) to read

$$\boxed{\begin{aligned} i\dot{\gamma}_a &= \frac{\lambda}{2} e^{i\Omega t} \gamma_b \\ i\dot{\gamma}_b &= \frac{\lambda}{2} e^{-i\Omega t} \gamma_a \end{aligned}} \tag{22}$$

where

$$\Omega = \omega - \omega_0 \tag{23}$$

Differentiating the first Eq with respect to time we get

$$\begin{aligned} i\ddot{\gamma}_a &= i\Omega \frac{\lambda}{2} e^{i\Omega t} \gamma_b + \frac{\lambda}{2} e^{i\Omega t} \dot{\gamma}_b \\ &= i\Omega (i\dot{\gamma}_a) + \frac{\lambda}{2} e^{i\Omega t} \left[-i \frac{\lambda}{2} e^{-i\Omega t} \gamma_a \right] \\ &= -\Omega \dot{\gamma}_a - i \frac{\lambda^2}{4} \gamma_a \end{aligned}$$

Thus

$$\boxed{\ddot{\gamma}_a - i\Omega \dot{\gamma}_a + \frac{\lambda^2}{4} \gamma_a = 0} \tag{24}$$

This is just like the Eq for the damped harmonic oscillator. To solve it we try the solution

$$\gamma_a = e^{ipt} \tag{25}$$

Then

$$-p^2 + \Omega p + \frac{\lambda^2}{4} = 0$$

so

$$p = \frac{\Omega}{2} \pm \frac{1}{2} \sqrt{\Omega^2 + \lambda^2} \tag{26}$$

If we define the Rabi frequency

$$\boxed{\omega_r = \sqrt{\Omega^2 + \lambda^2} = \sqrt{(\omega - \omega_0)^2 + (V_0/\hbar)^2}} \qquad (27)$$

The general solution is then

$$\boxed{\gamma_a(t) = e^{i\Omega t/2}\left[A\, e^{i\omega_r t/2} + B\, e^{-i\omega_r t/2}\right]} \qquad (28)$$

where A and B are constants.

To find γ_b we go back to (22)

$$i\dot{\gamma}_b = \frac{\lambda}{2}\, e^{-i\Omega t/2}\left[A\, e^{i\omega_r t/2} + B\, e^{-i\omega_r t/2}\right]$$

$$\dot{\gamma}_b = -\frac{i\lambda}{2}\left[A\, e^{-i(\Omega - \omega_r)t/2} + B\, e^{-i(\Omega + \omega_r)t/2}\right]$$

Integrating

$$\gamma_b = -\frac{i\lambda}{2}\left\{ A\, \frac{e^{-i(\Omega - \omega_r)t/2}}{-i\frac{(\Omega - \omega_r)}{2}} + B\, \frac{e^{-i(\Omega + \omega_r)t/2}}{-i\frac{(\Omega + \omega_r)}{2}} \right\}$$

Thus

$$\boxed{\gamma_b = e^{-i\Omega t/2}\left\{ \frac{\lambda A}{\Omega - \omega_r}\, e^{i\omega_r t/2} + \frac{\lambda B}{\Omega + \omega_r}\, e^{-i\omega_r t/2} \right\}} \qquad (29$$

Next we impose the initial conditions

$$\gamma_a(0) = 1 \qquad \gamma_b(0) = 0$$

Ne then get

$$\gamma_a(0) = A + B = 1$$

$$\gamma_b(0) = \frac{\lambda A}{\Omega - \omega_r} + \frac{\lambda B}{\Omega + \omega_r} = 0$$

ence

$$B = -A\left[\frac{\Omega + \omega_r}{\Omega - \omega_r}\right]$$

nd

$$A\left[\frac{\Omega - \omega_r - (\Omega + \omega_r)}{\Omega - \omega_r}\right] = 1$$

so

$$A = \frac{\omega_r - \Omega}{2\omega_r}$$

nd

$$B = \frac{\omega_r + \Omega}{2\omega_r}$$

The complete solution is, therefore

$$\boxed{\begin{aligned} \gamma_a(t) &= e^{i\Omega t/2}\left\{\frac{(\omega_r - \Omega)}{2\omega_r}\, e^{i\omega_r t/2} + \frac{(\omega_r + \Omega)}{2\omega_r}\, e^{-i\omega_r t/2}\right\} \\ \gamma_b(t) &= e^{-i\Omega t/2}\left\{-\frac{\lambda}{2\omega_r}\, e^{i\omega_r t/2} + \frac{\lambda}{2\omega_r}\, e^{-i\omega_r t/2}\right\} \end{aligned}} \qquad (30)$$

In particular we may write

$$\boxed{\gamma_b(t) = -\frac{i\lambda}{\omega_r}\, e^{-i\Omega t/2} \sin\left(\frac{\omega_r t}{2}\right)} \qquad (31)$$

and

$$\gamma_a(t) = e^{i\Omega t/2}\left\{ \cos\left(\frac{\omega_r t}{2}\right) - \frac{i\Omega}{\omega_r} \sin\left(\frac{\omega_r t}{2}\right)\right\} \qquad (32)$$

then

$$\boxed{|\gamma_b(t)|^2 = \frac{\lambda^2}{\omega_r^2} \sin^2\left(\frac{\omega_r t}{2}\right)} \qquad (33)$$

As a sanity check we also compute

$$|\gamma_a|^2 = \cos^2(\omega_r t/2) + \frac{\Omega^2}{\omega_r^2} \sin^2\left(\frac{\omega_r t}{2}\right)$$

thus

$$|\gamma_a|^2 + |\gamma_b|^2 = \cos^2(\omega_r t/2) + \underbrace{\frac{\Omega^2+\lambda^2}{\omega_r^2}}_{1} \sin^2(\omega_r t/2) = 1$$

the normalization is correct

In any case, our final result for the transition probability is

$$\boxed{P_t(a \to b) = |\gamma_b|^2 = \frac{\lambda^2}{\omega_r^2} \sin^2\left(\frac{\omega_r t}{2}\right)} \qquad (34)$$

where $\boxed{\omega_r^2 = (\omega - \omega_0)^2 + \lambda^2}$ (34')

It is common to have

$$\lambda = \frac{V_0}{\hbar} << |\omega - \omega_0|$$

so that we may approximate the Rabi frequency to

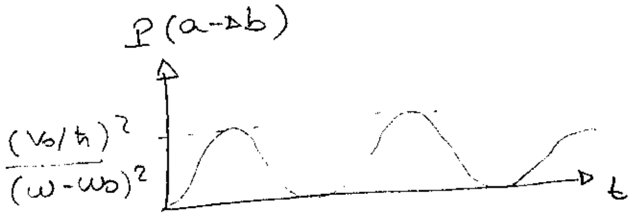
$$\omega_r = \sqrt{(\omega - \omega_0)^2 + (V_0/\hbar)^2} \approx |\omega - \omega_0| \tag{35}$$

In this case we get

$$\boxed{P_t(a \to b) \approx \frac{(V_0/\hbar)^2}{(\omega - \omega_0)^2} \sin^2\left[\frac{(\omega - \omega_0)t}{2}\right]} \tag{36}$$

this is a very famous and a very useful result

We see that the probability of transition is sinusoidal in t:



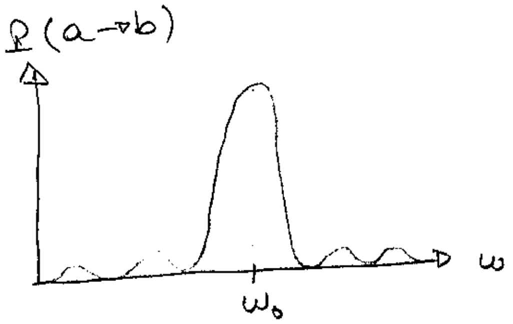
Since we are assuming V_0 is small, the maximum level will be much smaller than 1.

So, if you want to optimize your chance of obtaining a transition you shouldn't keep the perturbation on indefinitely. Instead, you should turn it off at time $t = \frac{\pi}{|\omega - \omega_0|}$, where P is a maximum.

Exactly at resonance, $\omega = \omega_0$, Eq (34) becomes

$$\boxed{P(a\to b) = \sin^2\left(\frac{\lambda t}{2}\right)} \qquad (37)$$

which is thus seen to reach the value 1. In practice it does not get this high because of the extra term we discarded in the rotating wave approximation. But this shows clearly why we call $\omega = \omega_0$ a resonance: the prob. of transition in this case is much larger. If we plot P as a function of ω for a given time t we get something like



Another important fact is this. If we repeat the same calculation, but starting with the opposite configuration

$$\psi_a(0) = 0 \qquad \psi_b(0) = 1$$

hen we arrive at the exact same result for $P(b\to a)$

$$\boxed{P_t(b\to a) = \frac{\lambda^2}{\omega_r^2}\sin^2\left(\frac{\omega_r t}{2}\right)} \qquad (38)$$

hus, the probability of the opposite transition is exactly he same.

To make sense of this let us go back to the ammonia molecule under the presence of a time-dependent electric field. The state $|a\rangle$ is the ground state. So Eq (34) says that there is a certain probability that the E-field will excite the molecule from E_a to E_b. For this to happen the molecule must have absorbed an energy

$$\Delta E = E_b - E_a = \hbar \omega_0$$

that is why we say it absorbed a photon, and this process is called absorption

However, Eq (38) also says that if the molecule is in the excited state, due to the interaction with the E-field it may also make a transition to the ground state. This was first discovered by Einstein and is called stimulated emission. It means that due to the interaction with photons, the molecule in an excited state may emit another photon with frequency ω_0. Thus, one photon comes in, 2 go out.

This is the idea behind amplification. I find a way of putting all molecules in my sample at the excited state, for instance using an electric current. Then 1 photon comes in, with stimulated emission it becomes 2, then 4, then 8, etc.

This is the working principle of a MASER: Microwave amplification by stimulated emission of radiation (the transmission of the NH_3 molecule is in the microwave region). The same thing occurs in a LASER. The only difference is that the transition is at optical frequencies.