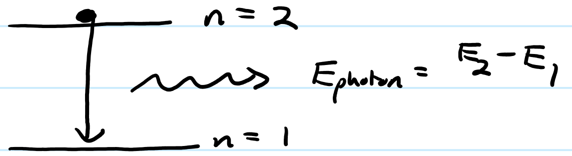
Time Dependent Perturbation Theory

References:
Griffiths 11.1 - 11.3
McIntyre 14.1 - 14.2

We've been talking about atomic transitions; suppose an electron in the $n=2$ state of Hydrogen jumps down (transitions) to $n=1$ and emits a photon



We know this happens, and we've been talking a lot about spectroscopy, but there's some nagging questions here... <u>why</u> does this happen?

For example, suppose $|\psi(0)\rangle = |210\rangle$, the $n=2, \ell=1, m=0$ state.

We know that $|\psi(t)\rangle = |210\rangle e^{\frac{-iE_2 t}{\hbar}}$ solves the full Schrödinger eqn

$$i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \quad \text{as is easily shown:}$$

$$i\hbar \frac{\partial}{\partial t}\left[|210\rangle e^{\frac{-iE_2 t}{\hbar}}\right] = \hat{H}\left[|210\rangle e^{-iE_2 t/\hbar}\right]$$

$$i\hbar |210\rangle \frac{\partial}{\partial t}\left[e^{-iE_2 t/\hbar}\right] = e^{-iE_2 t/\hbar}\hat{H}|210\rangle$$

$$i\hbar |210\rangle \left(\frac{-iE_2}{\hbar}\right) e^{\frac{-iE_2 t}{\hbar}} = e^{-iE_2 t/\hbar} E_2 |210\rangle$$

$$E_2 |210\rangle e^{-iE_2 t/\hbar} = E_2 |210\rangle e^{-iE_2 t/\hbar} \quad \checkmark$$

But if $|\psi(t)\rangle = |210\rangle e^{-iE_2 t/\hbar}$, what's the probability that at some later time that it will be in state $|100\rangle$?

$$P_{2\to 1} = |\langle 100|\psi(t)\rangle|^2 = \left|\langle 100|210\rangle e^{\frac{-iE_2 t}{\hbar}}\right|^2 = 0$$

by orthogonality this is zero.

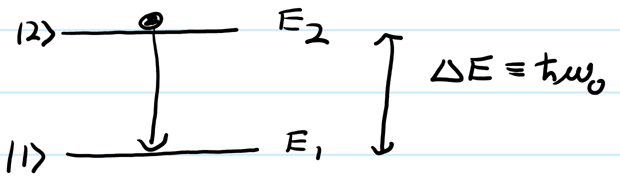
Once the atom is in an energy eigenstate, if left to its own devices, it will <u>stay</u> in that state. So why do transitions happen?

Time Dependent Perturbation Theory

The key point is that for some transition between levels to occur, we need to consider a time-dependent Hamiltonian.

Two-State System:

As an illustration, suppose we have a system with only two energy levels



the frequency of a photon emitted is ω_0.

Suppose we have a time dependent Hamiltonian, and we want to allow transitions between the states

If $\hat{H}$ is independent of time, $|\psi(t)\rangle = c_1|1\rangle e^{\frac{-iE_1t}{\hbar}} + c_2|2\rangle e^{\frac{-iE_2t}{\hbar}}$

with $|c_1|^2 + |c_2|^2 = 1$

The combination of eigenstates given by c_1 and c_2 does not change with time. All time dependence is carried in the exponents.

Now, suppose $\hat{H} = \hat{H}^0 + \hat{H}'(t)$ where $\hat{H}^0$ is a time-independent "unperturbed" piece, and $H'(t)$ is a small time dependent perturbation.

Caution: $\hat{H}'(t)$ is NOT a derivative. It's just a label meaning "different".

If we know how to solve $\hat{H}^0|\psi\rangle = E|\psi\rangle$, we can use these eigenstates as a basis.

$$|1\rangle \longrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |2\rangle \longrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\hat{H}^0 \longrightarrow \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \qquad \hat{H}'(t) \longrightarrow \begin{pmatrix} H'_{11}(t) & H'_{12}(t) \\ H'_{21}(t) & H'_{22}(t) \end{pmatrix}$$

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The state $|\psi(t)\rangle \longrightarrow \begin{pmatrix} c_1(t)\, e^{-iE_1t/\hbar} \\ c_2(t)\, e^{-iE_2t/\hbar} \end{pmatrix}$

Notice we're now allowing the combination of eigenstates to change with time. c_1 and c_2 depend on t.

The Schrödinger Equation Becomes:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \left[\hat{H}^0 + \hat{H}'(t)\right] |\psi(t)\rangle$$

$$i\hbar \begin{pmatrix} \dot{c}_1 e^{\frac{-iE_1t}{\hbar}} - \frac{iE_1}{\hbar} c_1 e^{\frac{-iE_1t}{\hbar}} \\ \dot{c}_2 e^{\frac{-iE_2t}{\hbar}} - \frac{iE_2}{\hbar} c_2 e^{\frac{-iE_2t}{\hbar}} \end{pmatrix} = \begin{pmatrix} E_1 + H_{11}' & H_{12}' \\ H_{21}' & E_2 + H_{22}' \end{pmatrix} \begin{pmatrix} c_1 e^{\frac{-iE_1t}{\hbar}} \\ c_2 e^{\frac{-iE_2t}{\hbar}} \end{pmatrix}$$

$$i\hbar \begin{pmatrix} \dot{c}_1 e^{\frac{-iE_1t}{\hbar}} \cancel{- \frac{iE_1}{\hbar} c_1 e^{\frac{-iE_1t}{\hbar}}} \\ \dot{c}_2 e^{\frac{-iE_2t}{\hbar}} \cancel{- \frac{iE_2}{\hbar} c_2 e^{\frac{-iE_2t}{\hbar}}} \end{pmatrix} = \begin{pmatrix} (\cancel{E_1} + H_{11}')c_1 e^{-iE_1t/\hbar} + H_{12}' c_2 e^{-iE_2t/\hbar} \\ H_{21}' c_1 e^{-iE_1t/\hbar} + (\cancel{E_2} + H_{22}')c_2 e^{-iE_2t/\hbar} \end{pmatrix}$$

multiply top eqn by $\frac{-i}{\hbar} e^{iE_1t/\hbar}$ and bottom by $\frac{-i}{\hbar} e^{iE_2t/\hbar}$

$$\begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = -\frac{i}{\hbar} \begin{pmatrix} H_{11}' c_1 + H_{12}' c_2 e^{-i(\Delta E)t/\hbar} \\ H_{21}' c_1 e^{+i(\Delta E)t/\hbar} + H_{22}' c_2 \end{pmatrix}$$

Recall $\Delta E = \hbar\omega_0$

$$\dot{c}_1 = \frac{-i}{\hbar}\left[H_{11}' c_1 + H_{12}' c_2 e^{-i\omega_0 t}\right]$$

$$\dot{c}_2 = \frac{-i}{\hbar}\left[H_{21}' c_1 e^{i\omega_0 t} + H_{22}' c_2\right]$$

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$$\boxed{\begin{aligned} \dot{c}_1 &= \frac{-i}{\hbar}\left[H'_{11}c_1 + H'_{12}c_2 e^{-i\omega_0 t}\right] \\ \dot{c}_2 &= \frac{-i}{\hbar}\left[H'_{21}c_1 e^{i\omega_0 t} + H'_{22}c_2\right] \end{aligned}}$$

Note, if there's no time dependence $\hat{H}' = 0$, then $\dot{c}_1 = \dot{c}_2 = 0$ and the c's are constant.

These two equations are equivalent to the original Schrödinger equation. Note, we haven't made any approximations yet. We just separated $\hat{H}$ into $\hat{H}^0$ and $\hat{H}'(t)$, and used the unperturbed states as a basis.

It's worth reminding that H'_{ij} are the matrix elements of H' in the <u>unperturbed</u> <u>basis</u>.

The boxed equations are two coupled differential equations. You can solve them, on occasion, but its usually very difficult to solve exactly. instead we assume $\hat{H}'$ is small so we can develop a series.

$$c_1(t) \approx c_1^{(0)} + \lambda c_1^{(1)} + \lambda^2 c_1^{(2)} + \dots$$

$$c_2(t) \approx c_2^{(0)} + \lambda c_2^{(1)} + \lambda^2 c_2^{(2)} + \dots$$

$$\hat{H}' \to \lambda \hat{H}'$$

the time dependent piece is first order in λ.

Insert this into the boxed equations and match powers of λ. The term which is first order in λ is:

$$\dot{c}_1^{(1)} = \frac{-i}{\hbar}\left[H'_{11}c_1^{(0)} + H'_{12}c_2^{(0)} e^{-i\omega_0 t}\right]$$

All factors of $\hat{H}'$ are first order in perturbation.

$$\dot{c}_2^{(1)} = \frac{-i}{\hbar}\left[H'_{21}c_1^{(0)} e^{i\omega_0 t} + H'_{22}c_2^{(0)}\right]$$

To use these equations
1. Specify $\hat{H}'$, the time dependent perturbation
2. Specify $c_1^{(0)}$ $c_2^{(0)}$, the initial state of the system
3. Solve for $c_1^{(1)}$ $c_2^{(1)}$. This gives you $|\Psi(t)\rangle$.

Example: "Spin Flip"

Suppose our system is an electron at rest in a $\vec{B}$-field $\vec{B} = B_0 \hat{k}$.

$$\hat{H}^0 = -\gamma \hat{\vec{S}} \cdot \vec{B} = -\gamma \hat{S}_z \cdot B_0 \qquad \text{where } \gamma = -\frac{e}{m}$$

$$\hat{H}^0 = \frac{e}{m} B_0 \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\frac{\hbar\omega_0}{2}$ ———— $|\uparrow\rangle$

$-\frac{\hbar\omega_0}{2}$ ———— $|\downarrow\rangle$

$\Delta E = \hbar\omega_0$ where ω_0 = Larmor Precession frequency $\frac{\hbar\omega_0}{2} = \frac{eB_0\hbar}{2m}$

$$\omega_0 = \frac{eB_0}{m} = |\gamma| B_0$$

At time $t=0$, the system is in the state $|\downarrow\rangle$. At time $t=0$ I turn on an additional $\vec{B}$-field $\vec{B} = B_x \hat{i}$, and at t_f I turn it off again. What is the spin state at time $t > t_f$?

$$\hat{H} = \hat{H}^0 + \frac{eB_x\hbar}{2m} \hat{S}_x \qquad \text{for} \qquad 0 < t < t_f$$

$$\hat{H} = \hat{H}^0 \qquad \text{otherwise.}$$

$$\hat{H}' = \begin{pmatrix} 0 & \hbar\omega \\ \hbar\omega & 0 \end{pmatrix} \quad \text{for } 0<t<t_f \qquad \text{where } \omega = \frac{eB_x}{2m}$$

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The equation from time dependent PT are:

$$\dot{c}_2^{(1)} = -\frac{i}{\hbar}\left[H'_{21}c_1^{(0)}e^{i\omega_0 t} + \cancelto{0}{H'_{22}c_2^{(0)}}\right]$$

In this case $|\chi(0)\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ so $c_1^{(0)}=1$, $c_2^{(0)}=0$

$$H' \to \hbar\omega\begin{pmatrix}0&1\\1&0\end{pmatrix}$$

The equations become:

$$\dot{c}_1^{(1)} = 0$$
$$\dot{c}_2^{(1)} = -\frac{i}{\hbar}\cdot\hbar\omega\cdot 1\cdot e^{i\omega_0 t}$$

$$c_2^{(1)} = -i\omega\int_0^{t_f} e^{i\omega_0 t} = -\frac{\omega}{\omega_0}\left[e^{i\omega_0 t_f}-1\right]$$

$$c_2^{(0)}+c_2^{(1)} = \frac{\omega}{\omega_0}\left[1-e^{i\omega_0 t_f}\right]$$

makes sense. If $t_f=0$, $c_2=0$

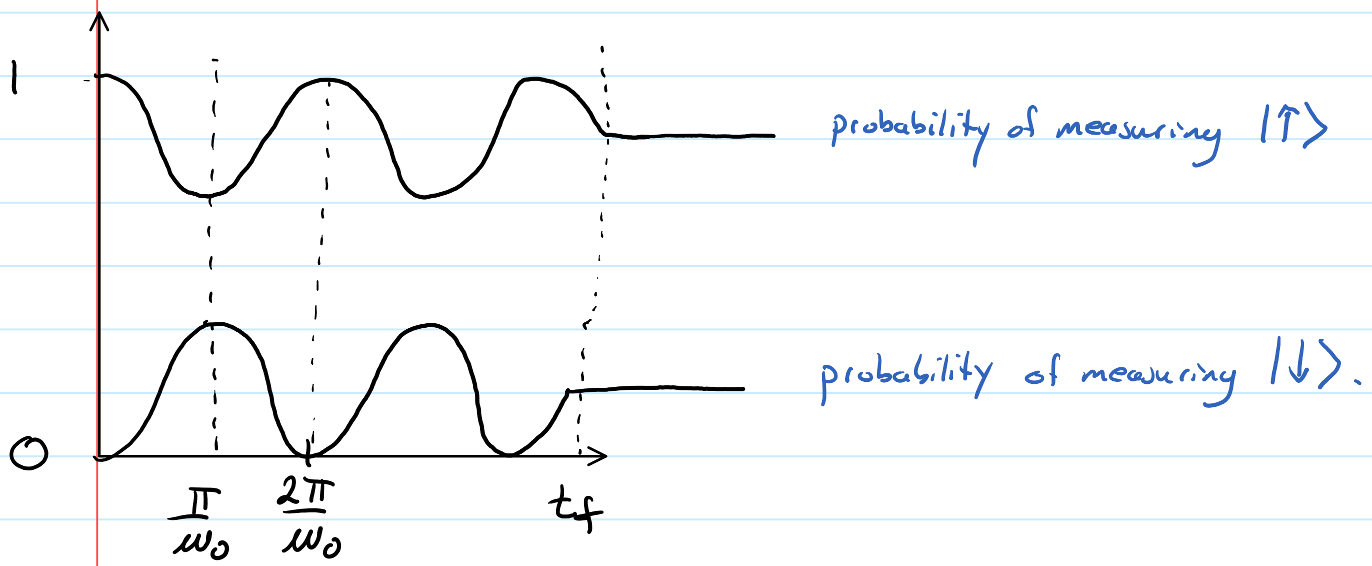
$$|c_2|^2 = \frac{\omega^2}{\omega_0^2}\left[1-e^{i\omega_0 t_f}\right]\left[1-e^{-i\omega_0 t_f}\right] = \frac{\omega^2}{\omega_0^2}\left[2-2\cos(\omega_0 t_f)\right]$$

$$|c_2|^2 = \frac{4\omega^2}{\omega_0^2}\sin^2\left(\frac{\omega_0 t_f}{2}\right) = \frac{4B_x^2}{B_0^2}\sin^2\left(\frac{\omega_0 t_f}{2}\right)$$

∴ The probability I'll measure the system with spin down at time t is $P_{down} = |c_2|^2 = \frac{4B_x^2}{B_0^2}\sin^2\left(\frac{\omega_0 t_f}{2}\right)$

To maximize the probability of a spin flip, choose $\frac{\omega_0 t_f}{2} = \frac{\pi}{2}$

$t_f = \pi/\omega_0$



Actually, we didn't even need time dependent PT to solve a problem like this ... we had HW problems on spin precession of this type already.

But, now let's move to a <u>truly</u> time dependent Hamiltonian.

Sinusoidal Perturbations

Example: "Rabi Flopping" [after Isador Rabi - Nobel Prize 1944]

Suppose our system is an electron at rest in a $\vec{B}$-field $\vec{B} = B_0 \hat{k}$.

$$\hat{H}^0 = -\gamma \hat{\vec{S}} \cdot \vec{B} = -\gamma \hat{S}_z \cdot B_0 \qquad \text{where } \gamma = -\frac{e}{m}$$

$$\hat{H}^0 = \frac{e}{m} B_0 \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\frac{\hbar\omega_0}{2}$ ———— $|\uparrow\rangle$

$-\frac{\hbar\omega_0}{2}$ ———— $|\downarrow\rangle$

$\Delta E = \hbar\omega_0$ where ω_0 = Larmor Precession frequency $\frac{\hbar\omega_0}{2} = \frac{eB_0\hbar}{2m}$

$$\omega_0 = \frac{eB_0}{m} = |\gamma| B_0$$

We now add an oscillating $\vec{B}$-field in the x-direction.

$\hat{H}' = \frac{e}{m} B_x \cdot \cos(\omega t) \hat{S}_x$ where ω is the oscillation frequency of the magnetic field.

$$\hat{H}' = \frac{eB_x\hbar}{2m} \cos(\omega t) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

We assume that $c_1^{(0)} = 1$, $c_2^{(0)} = 2$ so the system starts in the lower state.

The equation from time dependent PT is

$$\dot{c}_2^{(1)} = -\frac{i}{\hbar} \left[H'_{21} c_1^{(0)} e^{i\omega_0 t} + \overset{0}{\cancel{H'_{22} c_2^{(0)}}} \right]$$

$$\dot{c}_2^{(1)} = -\frac{i}{\hbar} \left[\frac{eB_x\hbar}{2m} \cos(\omega t) e^{i\omega_0 t} \right]$$

Time Dependent Perturbation Theory

$$\dot{c}_2^{(1)} = -\frac{i}{\hbar}\left[\frac{eB_x\hbar}{2m}\cos(\omega t)e^{i\omega_0 t}\right]$$

$$c_2^{(1)}(t) = -\frac{ieB_x}{2m}\int_0^t \cos(\omega t')e^{i\omega_0 t'}dt'$$

$$= -\frac{ieB_x}{2m}\int_0^t \frac{1}{2}\left[e^{i\omega t'}+e^{-i\omega t'}\right]e^{i\omega_0 t'}dt'$$

$$= -\frac{ieB_x}{4m}\left[\int_0^t\left(e^{i(\omega+\omega_0)t'}+e^{i(\omega_0-\omega)t'}\right)dt'\right.$$

$$= -\frac{ieB_x}{4m}\left[\frac{1}{i(\omega+\omega_0)}e^{i(\omega+\omega_0)t'}+\frac{1}{i(\omega_0-\omega)}e^{i(\omega_0-\omega)t'}\right]_0^t$$

$$c_2^{(1)}(t) = -\frac{eB_x}{4m}\left[\frac{e^{i(\omega+\omega_0)t}-1}{\omega+\omega_0}+\frac{e^{i(\omega_0-\omega)t}-1}{\omega_0-\omega}\right]$$

↑ ignore this.

Now, let's suppose $\omega \approx \omega_0$ so our oscillating frequency is near resonance. The second term dominates due to the small denominator.

Then, $$c_2^{(1)}(t) \cong -\frac{eB_x}{4m}\left[e^{\frac{i(\omega_0-\omega)}{2}t}\cdot\left(\frac{e^{\frac{i(\omega_0-\omega)t}{2}}-e^{-\frac{i(\omega_0-\omega)}{2}t}}{\omega_0-\omega}\right)\right]$$

$$\cong -\frac{eB_x}{4m}\left[e^{\frac{i(\omega_0-\omega)}{2}t}\cdot\frac{2i\sin\left(\frac{\omega_0-\omega}{2}t\right)}{\omega_0-\omega}\right]$$

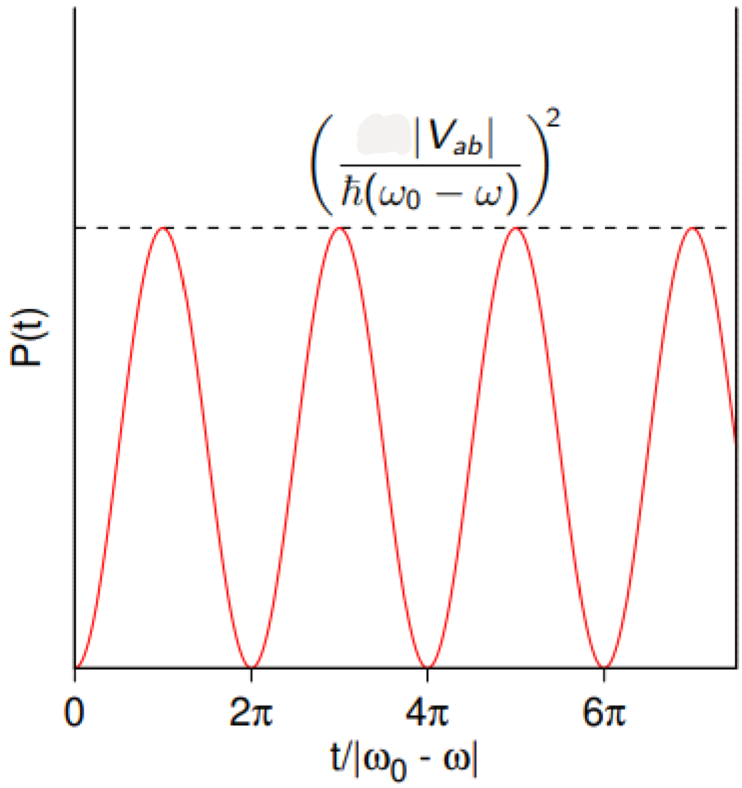
$$c_2^{(1)}(t) \cong -\frac{ieB_x}{2m}\left[e^{\frac{i(\omega_0-\omega)}{2}t}\cdot\frac{\sin\left(\frac{\omega_0-\omega}{2}t\right)}{\omega_0-\omega}\right]$$

And the probability of finding the particle in the upper state is

$$P = |c_2|^2 \cong \frac{e^2B_x^2}{4m^2}\left[\frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2}\right]$$

Time Dependent Perturbation Theory

Probability as a function of time

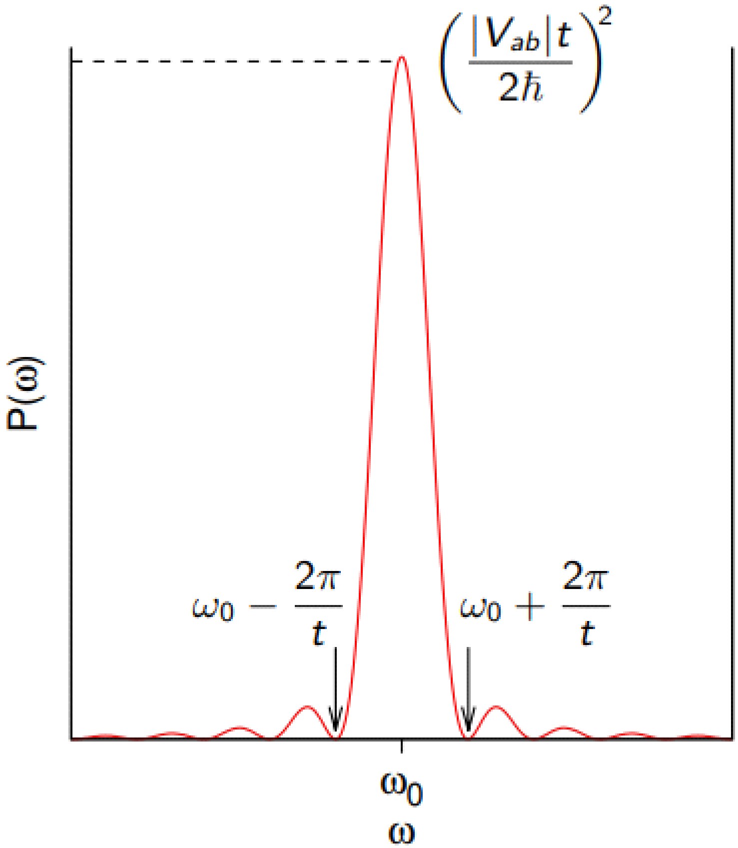


Note here $\hat{H}' = V \cdot \cos(\omega t)$

$V_{ab} \equiv \langle a | V | b \rangle$

In our case, $V_{ab} = \frac{eB_x \hbar}{2m}$

Transition probability as a function of frequency:



There is a strong peak at $\omega = \omega_0$. If the perturbation frequency is near the natural frequency, it is likely that a transition will take place.