How do we find $c_a(t)$ and $c_b(t)$? Requiring that the time DEPENDENT Sch. Eq. be satisfied.

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad H = H^0 + H'(t)$$

Recalling $\Psi(t) = c_a(t)\psi_a e^{-iE_a t/\hbar} + c_b(t)\psi_b e^{-iE_b t/\hbar}$

we simply plug this state into the Sch. Eq. above:

Time-independent Hamiltonian like usual hydrogen atom.

Perturbation is time dependent. It may be ~ sin(ωt) for example.

$$c_a[H^0\psi_a]e^{-iE_a t/\hbar} + c_b[H^0\psi_b]e^{-iE_b t/\hbar} + c_a[H'\psi_a]e^{-iE_a t/\hbar} + c_b[H'\psi_b]e^{-iE_b t/\hbar}$$

$$= i\hbar\left[\dot{c}_a\psi_a e^{-iE_a t/\hbar} + \dot{c}_b\psi_b e^{-iE_b t/\hbar} + c_a\psi_a\left(-\frac{iE_a}{\hbar}\right)e^{-iE_a t/\hbar} + c_b\psi_b\left(-\frac{iE_b}{\hbar}\right)e^{-iE_b t/\hbar}\right]$$

Time dependent coefficients.

The dot means $dc_a(t)/dt$ or $dc_b(t)/dt$.

Rewriting the formula we can notice some cancellations.

$$c_a[H^0\psi_a]e^{-iE_at/\hbar} + c_b[H^0\psi_b]e^{-iE_bt/\hbar} + c_a[H'\psi_a]e^{-iE_at/\hbar} + c_b[H'\psi_b]e^{-iE_bt/\hbar}$$
$$= i\hbar\Big[\dot{c}_a\psi_a e^{-iE_at/\hbar} + \dot{c}_b\psi_b e^{-iE_bt/\hbar}$$
$$+ c_a\psi_a\left(\frac{iE_a}{\hbar}\right)e^{-iE_at/\hbar} + c_b\psi_b\left(\frac{iE_b}{\hbar}\right)e^{-iE_bt/\hbar}\Big]$$

Then, the long original equation simplifies to:

$$c_a[H'\psi_a]e^{-iE_at/\hbar} + c_b[H'\psi_b]e^{-iE_bt/\hbar} = i\hbar\left[\dot{c}_a\psi_a e^{-iE_at/\hbar} + \dot{c}_b\psi_b e^{-iE_bt/\hbar}\right]$$

As often done, we will now exploit the orthogonality

$$\langle\psi_a|\psi_b\rangle = \delta_{ab}$$

Consider the inner product with $\langle\psi_a|$
and then the inner product with $\langle\psi_b|$:

Then, we obtain two equations:

$$c_a\langle\psi_a|H'|\psi_a\rangle e^{-iE_at/\hbar} + c_b\langle\psi_a|H'|\psi_b\rangle e^{-iE_bt/\hbar} = i\hbar\dot{c}_a e^{-iE_at/\hbar}$$

$$c_a\langle\psi_b|H'|\psi_a\rangle e^{-iE_at/\hbar} + c_b\langle\psi_b|H'|\psi_b\rangle e^{-iE_bt/\hbar} = i\hbar\dot{c}_b e^{-iE_bt/\hbar}$$

Reorder and use the following compact notation:

$$H'_{ij} \equiv \langle\psi_i|H'|\psi_j\rangle$$

$$\dot{c}_a = -\frac{i}{\hbar}\left[c_a H'_{aa} + c_b H'_{ab} e^{-i(E_b-E_a)t/\hbar}\right]$$

$$\dot{c}_b = -\frac{i}{\hbar}\left[c_b H'_{bb} + c_a H'_{ba} e^{i(E_b-E_a)t/\hbar}\right]$$

Note sign difference.

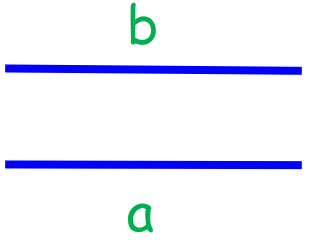
This system of two coupled equations for the coefficients $c_a(t)$ and $c_b(t)$ is totally equivalent to solving the time dependent Sch. Eq. for a two states system, even if H' is not small. **If you wish to include more states, then more equations are generated, as many as coefficients i.e. as many as states.**

Moreover, as you will see, often the diagonal matrix elements H'_{aa} and H'_{bb} are 0. E.g. an electric field arises from a potential that is "odd": $H' = -qE_0 z\cos(\omega t)$. "Diagonal" matrix elements will cancel.

Then, in practice often the system of equations simplifies further to:

$$\dot{c}_a = -\frac{i}{\hbar}H'_{ab}e^{-i\omega_0 t}c_b, \qquad \dot{c}_b = -\frac{i}{\hbar}H'_{ba}e^{i\omega_0 t}c_a.$$

where $\omega_0 \equiv \dfrac{E_b - E_a}{\hbar}$ with $E_b \geq E_a$, so $\omega_0 \geq 0$



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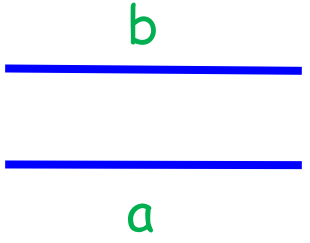


For "b", we find a nontrivial result:

$$\frac{dc_b^{(1)}}{dt} = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} \Rightarrow \boxed{c_b^{(1)} = -\frac{i}{\hbar} \int_0^t H'_{ba}(t') e^{i\omega_0 t'} \, dt'}$$

To obtain something nontrivial for the "a" state, we need another iteration in H':

$$\frac{dc_a^{(2)}}{dt} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} \left(-\frac{i}{\hbar}\right) \int_0^t H'_{ba}(t') e^{i\omega_0 t'} \, dt' \Rightarrow$$

$$\boxed{c_a^{(2)}(t) = 1 - \frac{1}{\hbar^2} \int_0^t H'_{ab}(t') e^{-i\omega_0 t'} \left[\int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} \, dt'' \right] dt'}$$

We could continue the process, but this is sufficient. Please read in book pages 406-407 the discussion about the normalization and the apparent problem that the normalization to 1 is not respected. But it is respected at the order of H' you are keeping.

11.1.3: Sinusoidal Perturbation

Consider, very common, perturbations where the space and time component are separated in factors:

$$H'(\mathbf{r}, t) = V(\mathbf{r})\cos(\omega t)$$

$$H'_{ab} = V_{ab}\cos(\omega t) \qquad V_{ab} \equiv \langle \psi_a | V | \psi_b \rangle$$

Then, in this case, at order 1, we find exactly for the *b* coefficient:

$$c_b(t) \cong -\frac{i}{\hbar} V_{ba} \int_0^t \cos(\omega t') e^{i\omega_0 t'}\, dt' = -\frac{i V_{ba}}{2\hbar} \int_0^t \left[e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'} \right] dt'$$

$$= -\frac{V_{ba}}{2\hbar} \left[\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} \right]$$

Another simplification. Work near resonance and drop the first term.

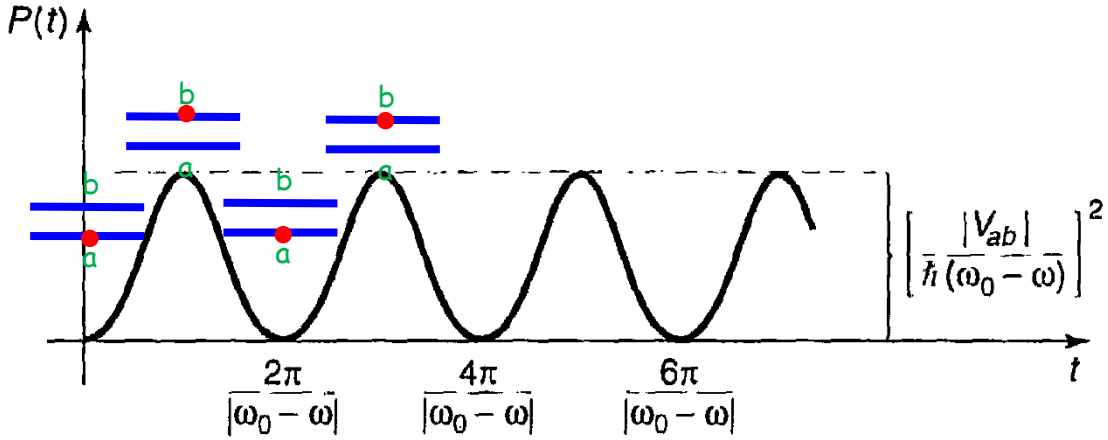
$$c_b(t) \cong -\frac{V_{ba}}{2\hbar}\frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega}\left[e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2}\right]$$

$$= -i\frac{V_{ba}}{\hbar}\frac{\sin[(\omega_0-\omega)t/2]}{\omega_0-\omega}e^{i(\omega_0-\omega)t/2}.$$

The transition probability for the transition from "a" to "b" is a sinusoidal function of time that can be large near resonance, even with a small perturbation V_{ba}.

$$P_{a\to b}(t) = |c_b(t)|^2 \cong \frac{|V_{ab}|^2}{\hbar^2}\frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

Note: sin(x)/(x) → 1 when x→0, so $\omega \to \omega_0$ is not a divergence.

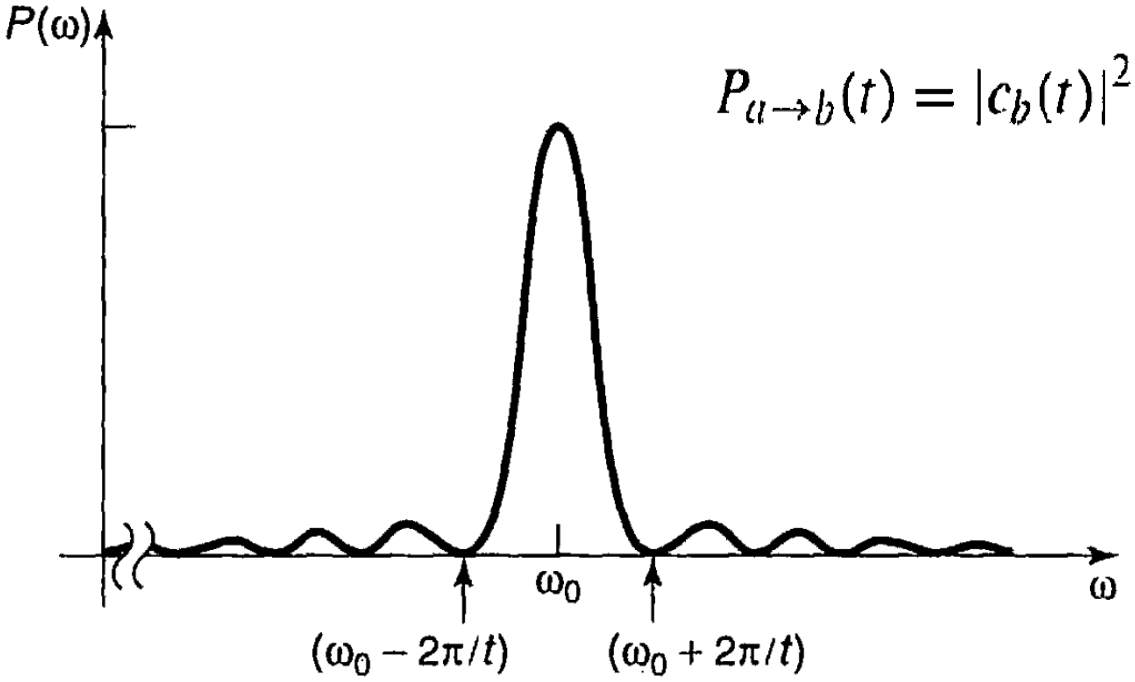


The amplitude, meaning how likely is the transition from "a" to "b", is regulated by both the perturbation strength hidden in V_{ba} and also by how close to resonance we are. If the amplitude exceeds 1, then the formula is too crude and needs to be improved …

Moreover, the probability is sinusoidal. The particle can absorb energy and go up, or release energy and come down.

At times $t_n = 2n\pi/|\omega_0 - \omega|$ where n=1,2,3, … the electron is back in the lower state "a" with 100% chance. Thus, often it is better to turn off the external field, after a time sufficient to excite the electron, if you wish to keep the electron in the upper state.

Plotting results at a fixed time, as a function of frequency, make more clear that near resonance the probability is maximized.



$$P_{a\to b}(t) = |c_b(t)|^2 \cong \frac{|V_{ab}|^2}{\hbar^2}\frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

Near resonance, $\sin^2[(\omega_0-\omega)t/2] \sim [\,(\omega_0-\omega)t/2\,]^2$

At resonance, amplitude grows like t^2 so eventually the transition will surely occur.