Chapter 11: Quantum Dynamics

Thus far, our potentials V(**r**) have been time independent. Now we will use V(**r**,t).

These type of problems are very difficult so we will work in the context of perturbation theory. The most dominant portion of *H* will be time independent, while only the perturbation will be time dependent.

By this procedure we will study the emission and absorption of radiation (photons) by an atom.

Thus far, we have casually spoken about transitions from high energy states to low. And you have learned about this since probably High School. But mathematically, if we are in an excited state, THUS FAR we stay there forever.

Then, how do we describe the transitions between levels, such as when an electron decays from a state, say, n=3 l=1 to the ground state n=1 l=0, by emitting a photon?

At the minimum, we have to "shake" a little bit the electron at n=3 l=1 to allow for the transition to occur. How do we shake the electron? By placing the electron in an external electromagnetic field, which often is time dependent. Then, "quantum jumps" – that are almost instantaneous – can occur.

11.1: Two-level systems

To study emission and absorption we need at least two states. Consider two eigenstates of H^0:

$$H^0 \psi_a = E_a \psi_a \qquad H^0 \psi_b = E_b \psi_b \qquad \langle \psi_a | \psi_b \rangle = \delta_{ab}$$

We will assume these two states are the only ones that really matter. Thus, any arbitrary state can be a linear combination of "a" and "b" at time t=0:

$$\Psi(0) = c_a \psi_a + c_b \psi_b \qquad |c_a|^2 + |c_b|^2 = 1$$

Again, you can imagine these two states as for example the 1s and 2p states of the hydrogen atom. Or they can be spinors up and down, describing a spin in a magnetic field.

If there is NO perturbation, you learned in the fall P411 that the time dependence is easy:

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

So far nothing new …

Now we will introduce a perturbation H'(t) that depends on time, such as an small external field.

The two original states are still a complete basis. But the time dependence is not so easy. We will consider the new time dependence by making the coefficients, that before were fixed numbers, time dependent...

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

We know ψ_a, ψ_b, E_a, and E_b. Thus, the challenge is to find the coefficients as a function of time.

For example if at time t=0, $c_a(0)$=1 and $c_b(0)$=0, then the electron is at "a" initially. If at a later time T the coefficients are $c_a(T)$=0 and $c_b(T)$=1 a transition occurred from ψ_a to ψ_b.

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

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

Time independent Hamiltonian like hydrogen atom.

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

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

$$= i\hbar\left[\dot{c}_a\psi_a e^{-iE_a t/\hbar} + \dot{c}_b\psi_b e^{-iE_b t/\hbar}\right.$$

$$\left. + c_a\psi_a\left(-\frac{iE_a}{\hbar}\right)e^{-iE_a t/\hbar} + c_b\psi_b\left(-\frac{iE_b}{\hbar}\right)e^{-iE_b t/\hbar}\right]$$

Time dependent coefficients.

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

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Rewriting the formula we can notice some cancellations.

$$c_a[H^0\psi_a]e^{-iE_at/\hbar} + c_b[H^0\psi_b]e^{-iE_bt/\hbar} + c_a[H'\psi_a]e^{-iE_at/\hbar} + c_b[H'\psi_b]e^{-iE_bt/\hbar}$$

$$= i\hbar\left[\dot{c}_a\psi_a e^{-iE_at/\hbar} + \dot{c}_b\psi_b e^{-iE_bt/\hbar}\right.$$

$$\left. + c_a\psi_a\left(\frac{iE_a}{\hbar}\right)e^{-iE_at/\hbar} + c_b\psi_b\left(\frac{iE_b}{\hbar}\right)e^{-iE_bt/\hbar}\right]$$

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:

$$c_a\langle\psi_a|H'|\psi_a\rangle e^{-iE_a t/\hbar} + c_b\langle\psi_a|H'|\psi_b\rangle e^{-iE_b t/\hbar} = i\hbar\dot{c}_a e^{-iE_a t/\hbar}$$

$$c_a\langle\psi_b|H'|\psi_a\rangle e^{-iE_a t/\hbar} + c_b\langle\psi_b|H'|\psi_b\rangle e^{-iE_b t/\hbar} = i\hbar\dot{c}_b e^{-iE_b t/\hbar}$$

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": $H' = -qE_0 z \cos(\omega t)$ .Then a "diagonal" matrix element involving odd or even functions will cancel.

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

$$\dot{c}_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t} c_b, \qquad \dot{c}_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t} c_a.$$
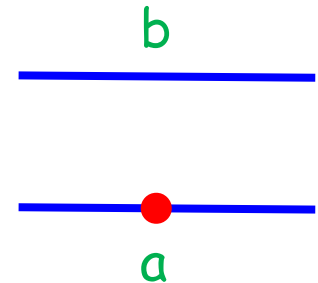
where $\quad \omega_0 \equiv \dfrac{E_b - E_a}{\hbar} \quad$ with $E_b \geq E_a$, so $\omega_0 \geq 0$

b
_____

a

8
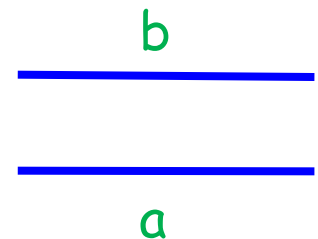
11.1.2: Time Dependent Perturbation Theory

It is only now that we will assume H' is "small". We will use an iterative process ...

Start with: $\quad c_a(0) = 1, \quad c_b(0) = 0$

b
_____

•
_____
a

If H' is zero, then all the matrix elements are zero, and this is the solution forever. The particle remains at state "a". $\quad c_a^{(0)}(t) = 1, \quad c_b^{(0)}(t) = 0$

Now insert the 0th-order values for the coefficients into the right of the pair of differential Eqs. of previous page:

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

For "a" nothing changes:

$$\frac{dc_a^{(1)}}{dt} = 0 \Rightarrow c_a^{(1)}(t) = 1$$

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 page 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, we find exactly at order 1 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}.

$$P_{a \to b}(t) = |c_b(t)|^2 \cong \frac{|V_{ab}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$
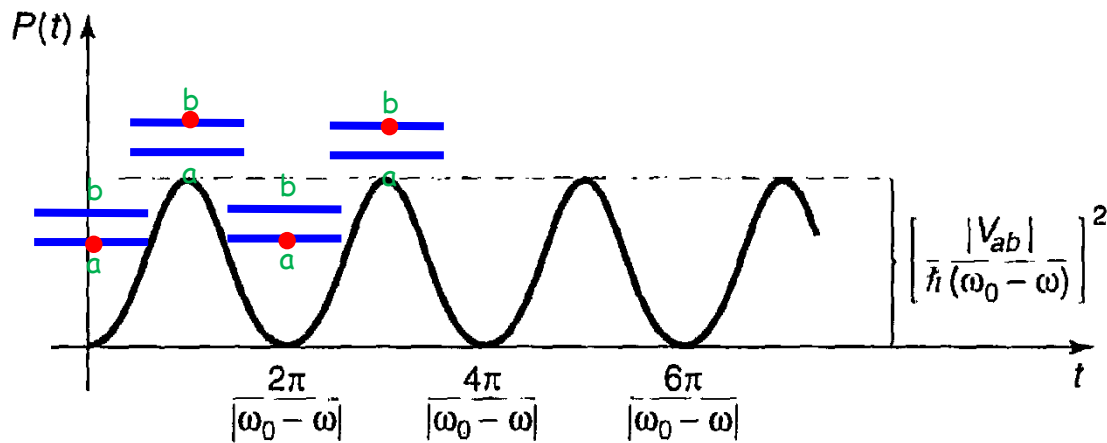
The amplitude, meaning how likely is the transition from "a" to "b", is regulated by both the perturbation strength hidden in V_{ba} and also by how close to resonance we are. If the amplitude exceeds 1, then the formula is too crude and needs to be improved ...

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.