Wave-matter interaction

Time-Dependent Perturbation Theory(introd.)

Everything we have done so far assumed the potential energy is a time independent function:

$V(\mathbf{r}, t) = V(r)$

and we have seen that in that case the T.D.S.E.: $i\hbar \frac{\partial \psi}{\partial t} = H\,\psi$

can be solved by separation of variables:

$$\psi(r, t) = \psi(r)\, e^{(-i E\, t/\hbar)}$$

With $\psi(r)$ solution of the T.I.S.E: $H\,\psi = E\,\psi$

Time-Dependent Perturbation Theory(introd.)

We know also that a general state of the system at t=0 can be written with some linear superposition of the eigenstates:

$$\psi(0) = \sum_m c_m \, \psi_m$$

Thus, the evolution of the system is written as:

$$\psi(t) = \sum_m c_m \, e^{(-i\, E_m \, t/\hbar)} \psi_m$$

Now, the probability of finding the system in state n at time t is

$$P_n(t) = |\langle\psi_n|\psi\rangle|^2 = |c_n \exp(-i \, E_n \, t/\hbar)|^2 = |c_n|^2 = P_n(0)$$

the probability of finding the system in state ψ_n at time t is exactly the same as the probability of finding the system in this state at the initial time t=0

Time-Dependent Perturbation Theory(introd.)

Now, the probability of finding the system in state n at time t is

$$P_n(t) = |\langle\psi_n|\psi\rangle|^2 = |c_n \exp(-i E_n t/\hbar)|^2 = |c_n|^2 = P_n(0)$$

the probability of finding the system in state ψ_n at time t is exactly the same as the probability of finding the system in this state at the initial time.

Because the time dependence of ψ is carried by the exponential factor ($e^{(-i E_m t/\hbar)}$), which cancels out in $|\psi|^2$, all probabilities and expectation values are constant in time.

In fact, we know that if the system is in one of his eigenstates then, in the absence of an external perturbation, it remains in this state for ever.

Time-Dependent Perturbation Theory(introd.)

In fact, We know that if the system is in one of his eigenstates then, in the absence of an external perturbation, it remains in this state for ever.

However, the presence of a small time-dependent perturbation can, in principle, give rise to a finite probability that if the system is initially in some eigenstate ψ_n of the unperturbed Hamiltonian then it is found in some other eigenstate at a subsequent time.

In this case, these states can be written as:

$$\psi(t) = \sum_m c_m(t)\, \exp(-i\, E_m\, t/\hbar)\, \psi_m$$

Where now the coefficient $c_m(t)$ are time dependent.

They depends on the time-dependent perturbation that we have turned on H'(t)

Time-Dependent Perturbation Theory(introd.)

$$\psi(t) = \sum_m c_m(t)\, \exp(-i\, E_m\, t/\hbar)\, \psi_m$$

Where now the coefficient $c_m(t)$ are time dependent.

They depends on the time-dependent perturbation that we have turned on H'(t) with :

$$\mathrm{H(t) = H_0 + H'(t)}$$

And hence also the probability to find the system in a certain state is time-dependent:

$$\mathrm{P_n(t) = |c_n(t)|^2}$$

Time-Dependent Perturbation Theory(introd.)

$$\psi(t) = \sum_m c_m(t)\, \exp(-i\, E_m\, t/\hbar)\, \psi_m$$

Where now the coefficient $c_m(t)$ are time dependent.

They depends on the time-dependent perturbation that we have turned on H'(t) with :

$$\mathrm{H(t)} = \mathrm{H_0} + \mathrm{H'(t)}$$

We can re-write the T.D.S.E. as:

$$i\,\hbar\, \frac{\partial\psi(t)}{\partial t} = H(t)\,\psi(t) = [H_0 + H'(t)]\,\psi(t)$$

Time-Dependent Perturbation Theory(introd.)

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$$\psi(t) = \sum_m c_m(t)\, \exp(-i\, E_m\, t/\hbar)\, \psi_m$$

in

We can re-write the T.D.S.E. as:

$$i\hbar \frac{\partial \psi(t)}{\partial t} = H(t)\,\psi(t) = [H_0 + H'(t)]\,\psi(t)$$

$$(H_0 + H')\,\psi = \sum_m c_m(t)\, \exp(-i\, E_m\, t/\hbar)\,(E_m + H')\,\psi_m$$

And also:

$$i\hbar \frac{\partial \psi}{\partial t} = \sum_m \left(i\hbar \frac{dc_m}{dt} + c_m E_m \right) \exp(-i\, E_m\, t/\hbar)\, \psi_m$$

Time-Dependent Perturbation Theory(introd.)

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T.D.S.E. $$i\hbar\,\frac{\partial\psi(t)}{\partial t} = [H_0 + H'(t)]\,\psi(t)$$

With $$(H_0 + H')\,\psi = \sum_m c_m(t)\;\exp(-i\,E_m\,t/\hbar)\,(E_m + H')\,\psi_m$$

And $$i\hbar\,\frac{\partial\psi}{\partial t} = \sum_m \left(i\hbar\,\frac{dc_m}{dt} + c_m\,E_m\right)\exp(-i\,E_m\,t/\hbar)\,\psi_m$$

Thus: $$\sum_m i\,\hbar\,\frac{dc_m}{dt}\,\exp(-i\,E_m\,t/\hbar)\,\psi_m = \sum_m c_m(t)\;\exp(-i\,E_m\,t/\hbar)\,H'\psi_m$$

To simplify this equation, let's focus on a two-state system where we have:

$$H_0\,\psi_1 = E_1\,\psi_1$$
$$H_0\,\psi_2 = E_2\,\psi_2$$

And:

$$\psi(t) = c_1(t)\;\exp(-i\,E_1\,t/\hbar)\,\psi_1 + c_2(t)\;\exp(-i\,E_2\,t/\hbar)\,\psi_2$$

Two-state system

$$\sum_m i\,\hbar \frac{dc_m}{dt} \exp(-i\,E_m\,t/\hbar)\,\psi_m = \sum_m c_m(t)\,\exp(-i\,E_m\,t/\hbar)\,H'\psi_m$$

To simplify this equation, let's focus on a two-state system where we have:

$$\psi(t) = c_1(t)\,\exp(-i\,E_1\,t/\hbar)\,\psi_1 + c_2(t)\,\exp(-i\,E_2\,t/\hbar)\,\psi_2$$

Then:

$$i\hbar \frac{dc_1}{dt} \exp(-i\,E_1\,t/\hbar)\,\psi_1 + i\hbar \frac{dc_2}{dt} \exp(-i\,E_2\,t/\hbar)\,\psi_2$$
$$= c_1(t)\exp(-i\,E_1\,t/\hbar)\,H'\psi_1 + c_2(t)\exp(-i\,E_2\,t/\hbar)\,H'\psi_2$$

Or in a more compact form :

$$i\hbar\left[\dot{c_1}\,e^{(-i\,E_1\,t/\hbar)}\psi_1 + \dot{c_2}e^{(-i\,E_2\,t/\hbar)}\psi_2\right] = c_1(t)e^{(-i\,E_1\,t/\hbar)}H'\psi_1 + c_2(t)e^{(-i\,E_2\,t/\hbar)}H'\psi_2$$

Two-state system

$$i\hbar\left[\dot{c}_1\, e^{(-i\,E_1\,t/\hbar)}\psi_1 + \dot{c}_2 e^{(-i\,E_2\,t/\hbar)}\psi_2\right] = c_1(t)e^{(-i\,E_1\,t/\hbar)}H'\psi_1 + c_2(t)e^{(-i\,E_2\,t/\hbar)}H'\psi_2$$

Let's apply the internal product with ψ_1:

$$i\hbar\langle\,\psi_1|\left[\dot{c}_1\, e^{(-i\,E_1\,t/\hbar)}\psi_1 + \dot{c}_2 e^{(-i\,E_2\,t/\hbar)}\psi_2\right]$$

$$= \langle\,\psi_1|\left[c_1(t)e^{(-i\,E_1\,t/\hbar)}H'\psi_1 + c_2(t)e^{(-i\,E_2\,t/\hbar)}H'\psi_2\,\right]$$

Then:

$$i\hbar\,\dot{c}_1\, e^{(-i\,E_1\,t/\hbar)} = c_1(t)e^{(-i\,E_1\,t/\hbar)}\langle\psi_1|H'|\psi_1\rangle + c_2(t)e^{(-i\,E_2\,t/\hbar)}\langle\psi_1|H'|\psi_2\rangle$$

Or in a more compact form :

$$\dot{c}_1 = -\frac{i}{\hbar}\left[c_1(t)H'_{11} + c_2(t)e^{-i\,(E_2-E_1\,)t/\hbar}H'_{12}\,\right]$$

n-states system

Thus:

$$\dot{c_1} = -\frac{i}{\hbar}\left[c_1(t)H'_{11} + c_2(t)e^{-i(E_2-E_1)t/\hbar}H'_{12}\right]$$

and

$$\dot{c_2} = -\frac{i}{\hbar}\left[c_2(t)H'_{22} + c_1(t)e^{i(E_2-E_1)t/\hbar}H'_{21}\right]$$

And in general for n-states:

$$\frac{dc_n(t)}{dt} = -\frac{i}{\hbar}\sum_m H'_{nm}(t)\ \exp(i\,\omega_{nm}\,t)\,c_m(t)$$

With $\omega_{nm} = \frac{E_n - E_m}{\hbar}$ and $H'_{nm}(t) = \langle n|H'(t)|m\rangle$

n-states system

And in general for n-states:

$$\frac{dc_n(t)}{dt} = -\frac{i}{\hbar}\sum_m H'_{nm}(t)\ \exp(i\,\omega_{nm}\,t)\,c_m(t)$$

- According to this equation, the time dependence of the set of N coefficients c_n, which specifies the probabilities of finding the system in these eigenstates at time t, is determined by N coupled first-order differential equations.
- If we would be able to find exact solution to this system of ODE we needed no approximations at all.
- Unfortunately, we cannot generally find exact solutions and we have to obtain approximate solutions.

Two-state system

Going back to the 2-state system:

$$\dot{c_1} = -\frac{i}{\hbar}\left[c_1(t)H'_{11} + c_2(t)e^{-i(E_2-E_1)t/\hbar}H'_{12}\right]$$

and

$$\dot{c_2} = -\frac{i}{\hbar}\left[c_2(t)H'_{22} + c_1(t)e^{i(E_2-E_1)t/\hbar}H'_{21}\right]$$

If $H'_{11}(t) = H'_{22}(t) = 0$ (this is typical)

Then:

$$\dot{c_1} = -\frac{i}{\hbar}c_2e^{-i\omega_0 t}H'_{12} \quad \text{and} \quad \dot{c_2} = -\frac{i}{\hbar}c_1e^{i\omega_0 t}H'_{21}$$

With $\omega_0 = \frac{E_2-E_1}{\hbar}$

Two-state system

Suppose that the particle starts out in the lower state:

$c_1(0) = 1$ and $c_2(0) = 0$

- Zeroth order approximation (no perturbation at all):

$c_1^{(0)}(t) = 1$ and $c_2^{(0)}(t) = 0$ (they would stay this way forever)

- First order:

  If we now put this $c_2^{(0)}(t)$ into $\dot{c}_1 = -\frac{i}{\hbar} c_2 e^{-i\,\omega_0 t} H'_{12}$

$$\frac{dc_1}{dt} \propto c_2 = 0 \;\Rightarrow\; c_1^{(1)}(t) = 1$$

And $c_1^{(0)}(t)$ in $\dot{c}_2 = -\frac{i}{\hbar} c_1 e^{i\,\omega_0 t} H'_{21}$

$$\frac{dc_2}{dt} = -\frac{i}{\hbar} e^{i\,\omega_0 t} H'_{21} \;\Rightarrow\; c_2^{(1)}(t) = -\frac{i}{\hbar}\int_0^t H'_{21}(t')\, e^{i\,\omega_0 t} dt'$$

Two-state system

- Zeroth order approximation (no perturbation at all):

$c_1^{(0)}(t) = 1$ and $c_2^{(0)}(t) = 0$ (they would stay this way forever)

- First order:

$$c_1^{(1)}(t) = 1$$

$$c_2^{(1)}(t) = -\frac{i}{\hbar}\int_0^t H'_{21}(t')\, e^{i\,\omega_0 t}\, dt'$$

Putting them back in the initial equations…

- Second order:

$$\frac{dc_1}{dt} = -\frac{i}{\hbar} e^{-i\,\omega_0 t} H'_{12} \left(-\frac{i}{\hbar}\right) \int_0^t H'_{21}(t')\, e^{i\,\omega_0 t}\, dt'$$

$$c_1^{(2)}(t) = -\frac{1}{\hbar^2}\int_0^t H'_{12}(t')\, e^{-i\,\omega_0 t'} \left[\int_0^{t'} H'_{21}(t'')\, e^{i\,\omega_0 t''}\, dt''\right] dt'$$

Two-state system

- Zeroth order approximation (no perturbation at all):

$c_1^{(0)}(t) = 1$ and $c_2^{(0)}(t) = 0$ (they would stay this way forever)

- First order:

$$c_1^{(1)}(t) = 1 \quad and \quad c_2^{(1)}(t) = -\frac{i}{\hbar}\int_0^t H'_{21}(t')\, e^{i\,\omega_0 t'} dt'$$

Putting them back in the initial equations...

- Second order:

$$c_1^{(2)}(t) = -\frac{1}{\hbar^2}\int_0^t H'_{12}(t')\, e^{-i\,\omega_0 t'}\left[\int_0^{t'} H'_{21}(t'')\, e^{i\,\omega_0 t''} dt''\right] dt'$$

While: $c_2^{(2)}(t) = c_2^{(1)}(t)$

Sinusoidal perturbations

Suppose that the perturbation has a sinusoidal time dependence:

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

so that $H'_{12} = V_{12}\cos(\omega t)$ $V_{12} \equiv \langle \psi_1 | V | \psi_2 \rangle$

The first order will give:

$$c_2^{(1)}(t) = -\frac{i}{\hbar} V_{21} \int_0^t \cos(\omega t')\, e^{i\omega_0 t'} dt' =$$

$$= -\frac{i}{2\hbar} V_{21} \int_0^t \left[e^{i(\omega_0+\omega)t'} + e^{i(\omega_0-\omega)t'} \right] dt'$$

$$= -\frac{V_{21}}{2\hbar} \left[\frac{e^{i(\omega_0+\omega)t} - 1}{(\omega_0+\omega)} + \frac{e^{i(\omega_0-\omega)t} - 1}{(\omega_0-\omega)} \right]$$

Sinusoidal perturbations

Suppose that the perturbation has a sinusoidal time dependence:

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

so that $H'_{12} = V_{12}\cos(\omega t)$ $\quad V_{12} \equiv \langle \psi_1 | V | \psi_2 \rangle$

The first order will give:

$$c_2^{(1)}(t) = -\frac{V_{21}}{2\hbar}\left[\frac{e^{i(\omega_0+\omega)t}-1}{(\omega_0+\omega)} + \frac{e^{i(\omega_0-\omega)t}-1}{(\omega_0-\omega)}\right]$$

If we restrict our attention to ω_0 that are very close to ω the second term in the square brackets dominates:

Sinusoidal perturbations

Suppose that the perturbation has a sinusoidal time dependence:

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

so that $H'_{12} = V_{12}\cos(\omega t)$ $\quad V_{12} \equiv \langle \psi_1 | V | \psi_2 \rangle$

The first order will give (for ω_0 that are very close to ω):

$$c_2^{(1)}(t) = -\frac{V_{21}}{2\hbar}\left[\frac{e^{i(\omega_0-\omega)t}-1}{(\omega_0-\omega)}\right]$$

That can be also written as:

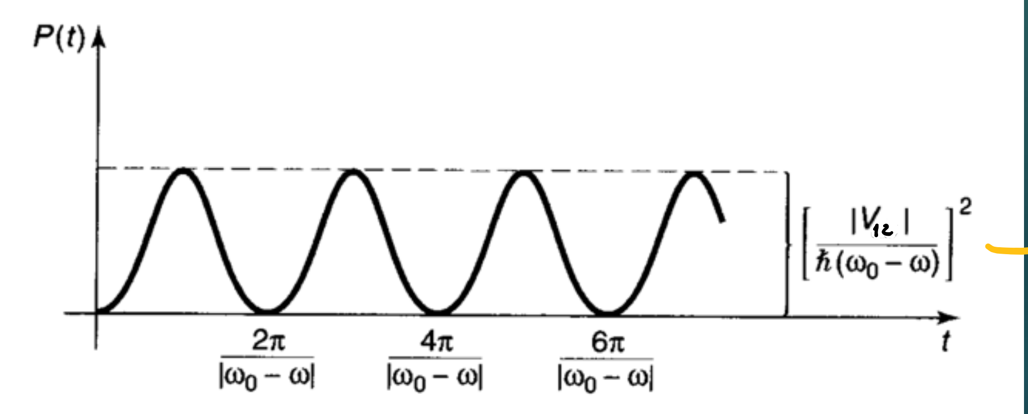
$$c_2^{(1)}(t) = -i\frac{V_{21}}{\hbar}\frac{\sin[(\omega_0-\omega)t/2]}{(\omega_0-\omega)}e^{i(\omega_0-\omega)t/2}$$

Sinusoidal perturbations

$$c_2^{(1)}(t) = -i\frac{V_{21}}{\hbar}\frac{sin[(\omega_0-\omega)t/2]}{(\omega_0-\omega)}e^{i(\omega_0-\omega)t/2}$$

The transition probability, the probability that a particle which started out in the state ψ_1 will be found, at time t, in the state ψ_2 is:

$$P_{1\to2}(t) = \frac{|V_{21}|^2}{\hbar^2}\frac{sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$



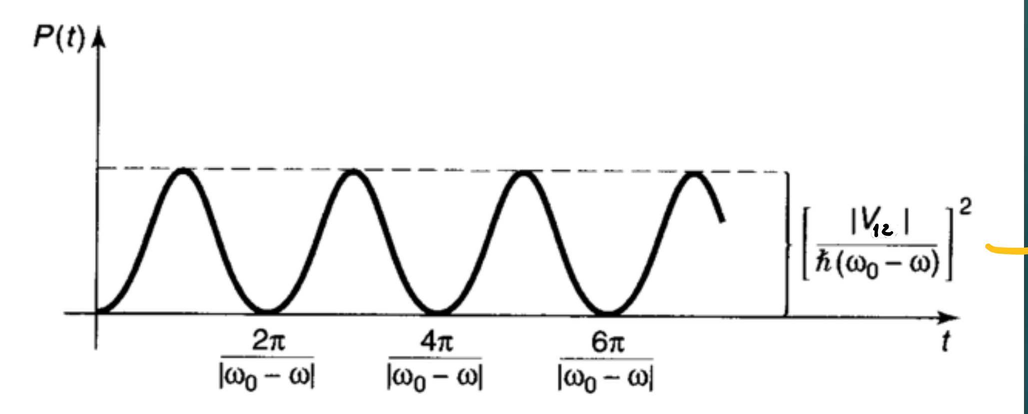
Must still be very "small"

Sinusoidal perturbations

The transition probability, the probability that a particle which started out in the state ψ_1 will be found, at time t, in the state ψ_2 is:

$$P_{1\to 2}(t) = \frac{|V_{21}|^2}{\hbar^2}\frac{sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

The most remarkable feature of this result is that, as a function of time, the transition probability oscillates sinusoidally.



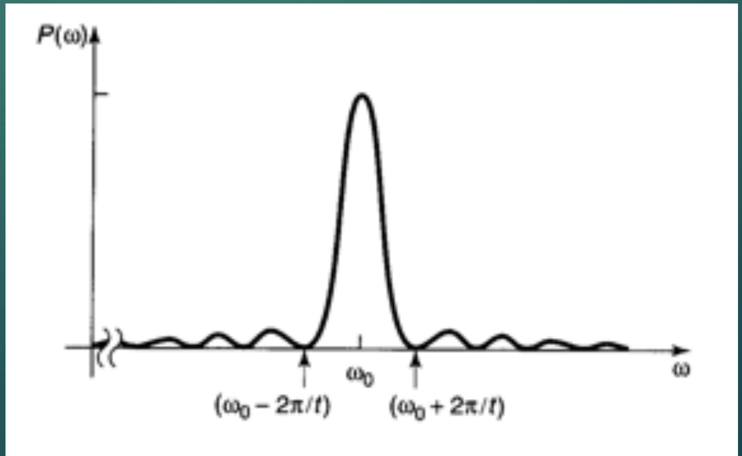
Must still be very "small"

Sinusoidal perturbations

$$c_2^{(1)}(t) = -i\frac{V_{21}}{\hbar}\frac{sin[(\omega_0-\omega)t/2]}{(\omega_0-\omega)}e^{i(\omega_0-\omega)t/2}$$

The transition probability, the probability that a particle which started out in the state ψ_1 will be found, at time t, in the state ψ_2 is:

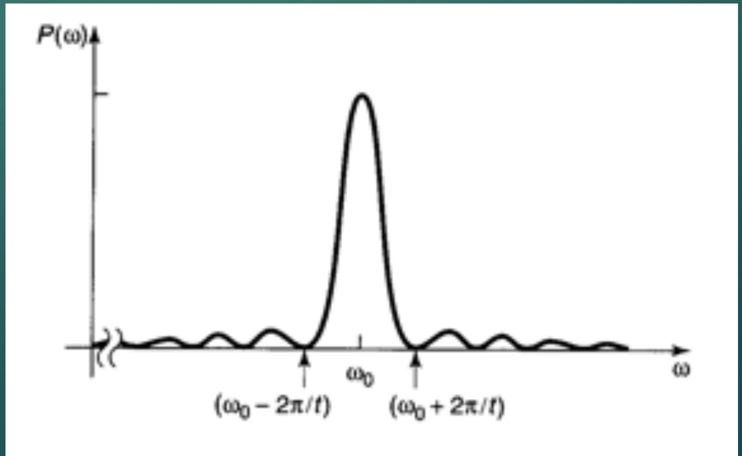
$$P_{1\to2}(t) = \frac{|V_{21}|^2}{\hbar^2}\frac{sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$



Sinusoidal perturbations

If you want to maximize your chances of provoking a transition, you should not keep the perturbation on for a long period: You do better to turn it off' after a time $\frac{\pi}{(\omega_0-\omega)}$, and hope to "catch" the system in the upper state.

$$P_{1\to 2}(t) = \frac{|V_{21}|^2}{\hbar^2}\frac{sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$



Electric dipole approximation

An electromagnetic wave (such as light) consists of oscillating electric and magnetic fields. An atom, in the presence of a passing light wave, responds primarily to the electric component, a sinusoidally oscillating electric field:

$$E(r,t) = E_0 \cos(K \cdot r - \omega t)$$

If the wavelength is long (compared to the size of the atom), we can ignore the spatial variation in the field:

$$|K \cdot r| \ll 1$$

in fact $|K| = \frac{2\pi}{\lambda} \Rightarrow |K \cdot r| \sim \frac{r}{\lambda} \ll 1$

$r \sim 1\,\text{Å}$

$\lambda \sim 5000\,\text{Å}$ in visible range

Then

$$E(r,t) = E_0 \left(\cos(K \cdot r) \cos(\omega t) + \sin(\omega t) \sin(K \cdot r) \right)$$

$\cos(K \cdot r) \approx 1$, $\sin(K \cdot r) \approx K \cdot r$

Electric dipole approximation

If the wavelength is long (compared to the size of the atom), we can ignore the spatial variation in the field:

$|K \cdot r| << 1$ in fact $|K| = \frac{2\pi}{\lambda} \Rightarrow |K \cdot r| \sim \frac{r}{\lambda} << 1$

$r \sim 1$ Å
$\lambda \sim 5000$ Å in visible range

Then

$E(r,t) = E_0 \left[\cos(K \cdot r) \cos(\omega t) + \sin(\omega t) \sin(K \cdot r) \right]$

$\cos(K \cdot r) \approx 1$, $\sin(K \cdot r) \approx K \cdot r$

$\Rightarrow E(r,t) = \left[\cos \omega t + (K \cdot r) \sin \omega t \right] E_0$

0^{th} order approximation:

$E(r,t) = E_0 \cos(\omega t) \, \hat{z}$

if the polarization is along z-direction

Emission and absorption of radiation

An electromagnetic wave (such as light) consists of oscillating electric and magnetic fields. An atom, in the presence of a passing light wave, responds primarily to the electric component, a sinusoidally oscillating electric field:

$$E(z,t) = E_0 (\cos \omega t)\ \hat{z}$$

The associated energy (providing the perturbing Hamiltonian) is:

$$H' = -q \int E \cdot dz = -q E_0 z \cos(\omega t)$$

q is the electron charge

the dipole moment $p = q \cdot z$ → here $p = q \langle \psi_2 | z | \psi_1 \rangle$

Thus:

$$H'_{21} = -p E_0 \cos(\omega t)$$

Emission and absorption of radiation

An electromagnetic wave (such as light) consists of oscillating electric and magnetic fields. An atom, in the presence of a passing light wave, responds primarily to the electric component, a sinusoidally oscillating electric field:

$$E(z,t) = E_0 (\cos \omega t)\ \hat{z}$$

The associated energy (providing the perturbing Hamiltonian) is:

$$H'_{21} = -p E_0 \cos(\omega t)$$

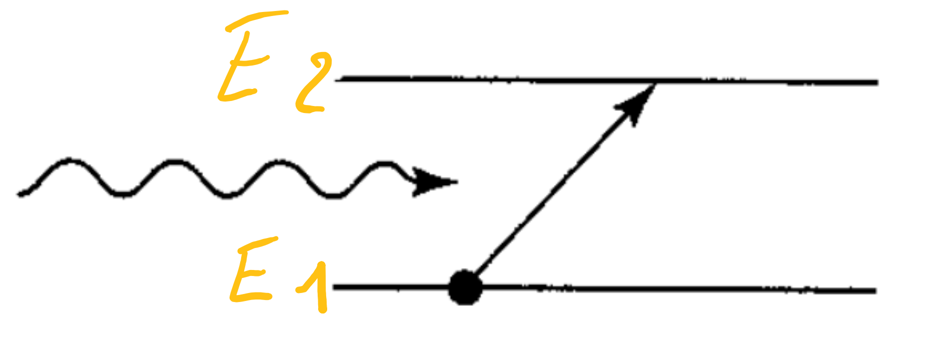
With the perturbation potential:

$$V_{21} = -p E_0$$

$$\Rightarrow \quad H'_{21} = V_{21} \cos(\omega t)$$

as considered before!

Emission and absorption of radiation



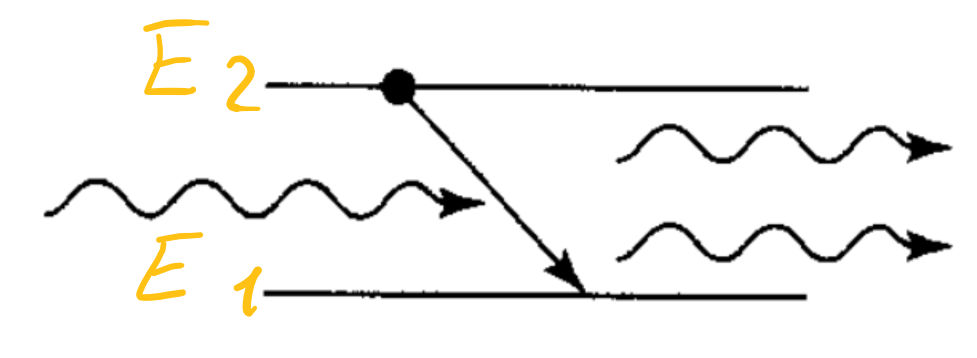
(a) Absorption

If an atom starts out in the "lower" state ψ_1, and you shine a polarized monochromatic beam of light on it, the probability of a transition to the "upper" state ψ_2 is given by:

$$P_{1\to 2}(t) = \left(\frac{pE_0}{\hbar}\right)^2 \frac{sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

In this process, the atom absorbs a photon or in a more precise formalism, the atom absorbs an energy $E_2 - E_1 = \hbar\omega_0$

Emission and absorption of radiation

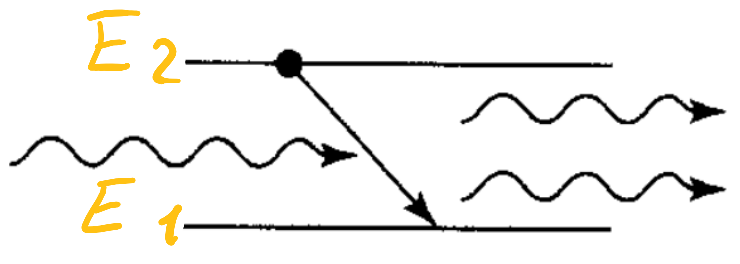


(b) Stimulated emission

But, if an atom starts out in the "higher" state ψ_2, the probability of a transition to the "lower" state ψ_1 is given by:

$$P_{2\to 1}(t) = \left(\frac{pE_0}{\hbar}\right)^2 \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$

Emission and absorption of radiation



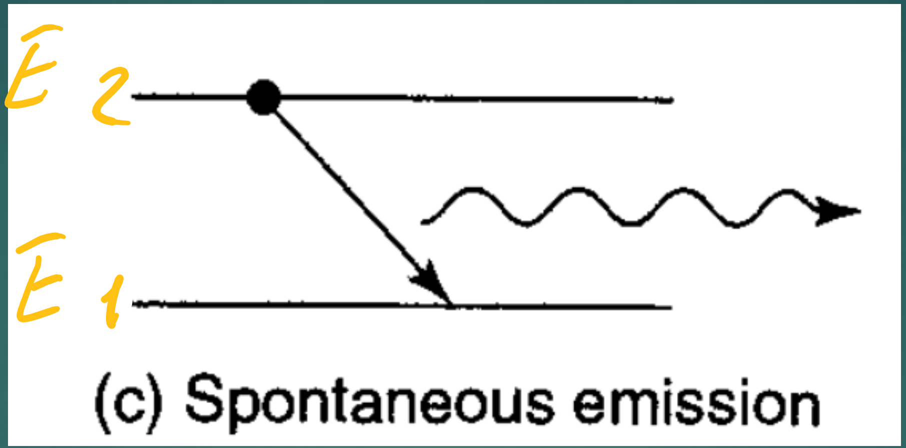
(b) Stimulated emission

If the particle is in the upper state, and you shine light on it, it can make a transition to the lower state, and in fact the probability of such a transition is exactly the same as for a transition upward from the lower state.

This process, which was first discovered by Einstein, is called stimulated emission.

In the case of stimulated emission, the electromagnetic field gains energy $\hbar\omega_0$ from the atom: one photon went in and two photons came out!

Emission and absorption of radiation



There is a third mechanism by which radiation interacts with matter; it is called spontaneous emission. Here an atom in the excited state makes a transition downward, with the release of a photon but without any applied electromagnetic field to initiate the process.

This is the mechanism that accounts for the normal decay of an atomic excited state. There is no external perturbation, but the "zero-point" radiation serves to activate the spontaneous emission.