Hydrogen-like systems

Replace the proton with a heavy nucleus with charge $Z|e|$.

$$H = \frac{p^2}{2m} - \frac{Ze^2}{R}$$

nearly unchanged, if $m_N \gg m_e$.

$Z = 1$ for H, 2 for He^+, 3 for Li^{2+}, etc.

For multi-electron atoms, Z can be used (approximately) for the inner-shell (K-shell) electrons. For outer shell electrons, $Z_{eff} < Z$.

For first approximation, take $e^2 \to Ze^2$.

Recall $a_0 = \frac{\hbar^2}{me^2}$, so $a_0 \to \frac{a_0}{Z}$ (gets smaller with larger Z).

Energy levels: $-\frac{e^2}{2a_0 n^2} \to -\frac{Z^2 e^2}{2a_0 n^2}$

$$\Delta E_{fine} \sim \alpha^2\left(\frac{e^2}{2a_0}\right) \to Z^4\alpha^2\left(\frac{e^2}{2a_0}\right)$$

$$\Delta E_{HF} \sim g_p\alpha^2\left(\frac{e^2}{2a_0}\right) \to Z^3 g_N \alpha^2\left(\frac{e^2}{2a_0}\right) \qquad (g_p|e| \to g_N|e|)$$

But, proton had $I = 1/2$; other nuclei have different I.

- ^2H (deuteron) has $I = 1$
- ^{12}C and ^{16}O have $I = 0$
- ^{14}N has $I = 1$
- ^{35}Cl has $I = 3/2$
- ^{17}O has $I = 5/2$

Also, many nuclei (including ^2H) have electric quadrupole moments.
Contributes comparably to nucleus magnetic dipole moment.

$$\Delta E_{Lamb} \sim \frac{\alpha^3}{n^3}\left(\frac{e^2}{2a_0}\right) \to \frac{\alpha^3}{n^3}\left(\frac{Z^2 e^2}{2a_0}\right)$$

Time-dependent perturbation theory

Typical questions:

* Shine light on an atom. $\frac{\text{Probability}}{\text{time}}$ atom is ionized?
* Atom in an excited state. $\frac{\text{Probability}}{\text{time}}$ atom emits photon, falls to a lower state?
* Apply voltage to a metal. How much current produced?

$$H(t) = \underbrace{H_0}_{\text{"simple"}} + \underbrace{V(t)}_{\text{"small"}}.$$

Use the interaction picture:

$$|\Psi(t)\rangle_I = e^{iH_0 t/\hbar}\, |\Psi(t)\rangle$$ ← Schrodinger picture ket

For any observable operator A,

$$A_I = e^{iH_0 t/\hbar} A\, e^{-iH_0 t/\hbar}$$

At $t=0$, $|\Psi(t)\rangle_I = |\Psi(t)\rangle$ and $A_I = A$.

Time evolution:

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle_I = V_I\, |\Psi(t)\rangle_I$$

$$\frac{d}{dt} A_I = \frac{1}{i\hbar}[A_I, H_0]$$

(Special case: Heisenberg picture if $V_I = V = 0$.)

Solution: $|\Psi(t)\rangle_I = U_I(t,t_0)\, |\Psi(t_0)\rangle_I$, where:

$$U_I(t,t_0) = T\left[\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} V_I(t')\, dt'\right)\right]$$

T ← time-ordered product

$$= 1 + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} V_I(t')\,dt' + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, V_I(t')\, V_I(t'')$$

$$+ \left(\frac{-i}{\hbar}\right)^3 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt'''\, V_I(t')\, V_I(t'')\, V_I(t''') + \ldots$$

Hope this converges. Usually use only terms linear or quadratic in V_I.

Suppose we want transition probability $|i\rangle \to |n\rangle$.

Assume these are eigenstates of H_0 with eigenvalues E_i and E_n.

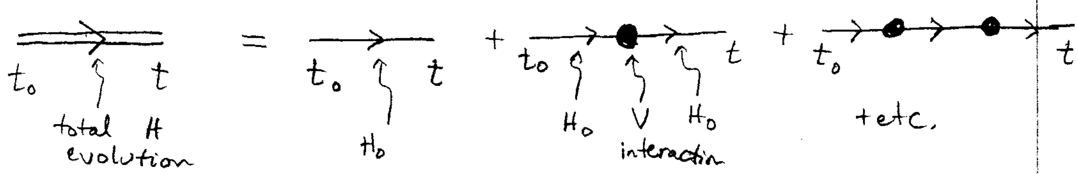
Define $c_n(t) = \langle n | U_I(t, t_0) | i \rangle = c_n^{(0)}(t) + c_n^{(1)}(t) + c_n^{(2)}(t) + \ldots$

Also, let $\omega_{ni} = \dfrac{E_n - E_i}{\hbar}$, and $V_{nm} = \langle n | V | m \rangle$.

Note no I.

Then
$$c_n^{(0)} = \delta_{ni}$$
$$c_n^{(1)} = -\frac{i}{\hbar} \int_{t_0}^{t} e^{i\omega_{ni} t'} V_{ni}(t')\, dt'$$
$$c_n^{(2)} = \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t''} dt'' \sum_m e^{i\omega_{nm} t'} V_{nm}(t')\, e^{i\omega_{mi} t''} V_{mi}(t'')$$

Interpretation:

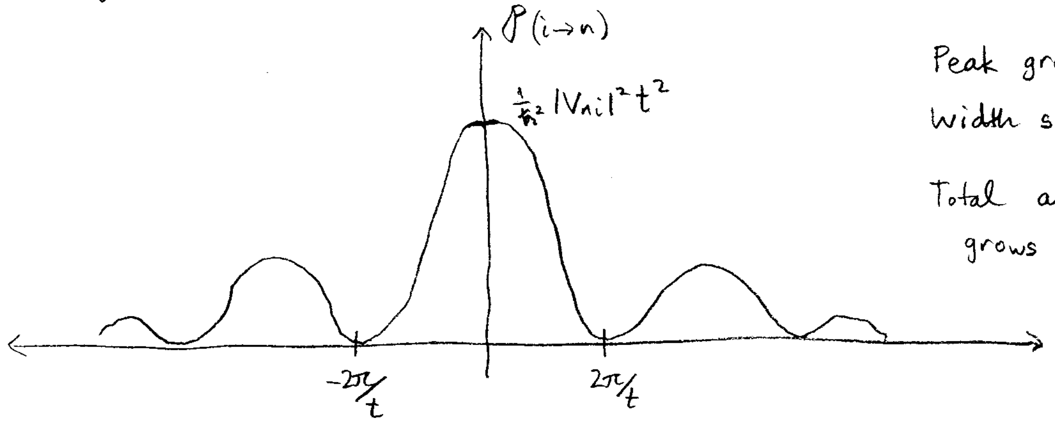


$$P(i \to n) = |c_n^{(1)}(t) + c_n^{(2)}(t) + \ldots|^2$$

Constant perturbation:
$$V(t) = \begin{cases} 0 & (t < 0) \\ V & (t > 0) \end{cases}$$

then
$$P(i \to n) \simeq |c_n^{(1)}|^2 = \begin{cases} \dfrac{4|V_{ni}|^2}{\hbar^2 \omega_{ni}^2} \sin^2\left(\dfrac{\omega_{ni} t}{2}\right) & (\text{for } \omega_{ni} \neq 0) \\[2ex] \dfrac{1}{\hbar^2} |V_{ni}|^2 t^2 & (\text{for } \omega_{ni} = 0) \end{cases}$$

Assuming ω_{ni} is continuous. For fixed t:



Peak grows $\sim t^2$

Width shrinks $\sim \dfrac{1}{t}$

Total area $\sim \dfrac{2\pi}{\hbar} t$ grows linearly with time.

Consider a group of final states $|n\rangle$ such that

* $E_n \approx E_i$ for all
* $|V_{ni}|^2$ doesn't change violently within the group.

Then $\sum_n P_{i\to n}(t) = \Gamma t$, where

$$\boxed{\Gamma = \underset{\substack{\uparrow \\ \text{Sakurai's notation}}}{w_{i\to n}} = \frac{2\pi}{\hbar} |V_{ni}|^2 \rho(E_n)\Big|_{E_n \approx E_i}}$$

where the number of states between E and $E+dE$ is $\rho(E)\,dE$.

Sakurai writes $\overline{|V_{ni}|^2}$ ← reminder that all $|V_{ni}|^2$ in the group must be nearly same.

or $$\boxed{w_{i\to n} = \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i)}$$ ← need to integrate $\int dE_n$

Either is <u>Fermi's Golden Rule</u> (invented by Dirac).

Restrictions: Need $t \ll \frac{2\pi\hbar}{\delta E}$ where δE = typical splitting between neighboring E_n's, if not continuous.

Otherwise, won't have enough states under the bump.

Need $\Gamma t < 1$. (Probability can't be ≥ 1)

Need t large enough to cover the spread in E_n that you are looking at: $t > \frac{2\pi\hbar}{\Delta E_n}$ ($\Delta E_n = E_{n,max} - E_{n,min}$ for group.)

For 2nd-order transitions:

$$w_{i\to n} = \frac{2\pi}{\hbar} \left| V_{ni} + \sum_m \frac{V_{nm}V_{mi}}{E_i - E_m} \right|^2 \delta(E_n - E_i).$$

Another important case:

$V(t) = \tilde{V} e^{i\omega t} + \tilde{V}^\dagger e^{-i\omega t}$ = harmonic perturbation (includes sines and cosines).

Result is very similar to the constant case:

$$W_{i\to n} = \frac{2\pi}{\hbar}|\tilde{V}_{ni}|^2 \rho(E_n)\Big|_{E_n \simeq E_i - \hbar\omega} \qquad \text{if } E_n < E_i$$

$$W_{i\to n} = \frac{2\pi}{\hbar}|\tilde{V}_{ni}|^2 \rho(E_n)\Big|_{E_n \simeq E_i + \hbar\omega} \qquad \text{if } E_n > E_i$$

So $$W_{i\to n} = \frac{2\pi}{\hbar}|\tilde{V}_{ni}|^2\Big[\delta(E_n - E_i + \hbar\omega) + \delta(E_n - E_i - \hbar\omega)\Big].$$

(Note $|\tilde{V}_{ni}|^2 = |\tilde{V}_{ni}^{\dagger}|^2$.)

stimulated emission of energy $\hbar\omega$ from $\tilde{V}$.

absorbs energy $\hbar\omega$ from $\tilde{V}$

As before, should include only states with similar $|\tilde{V}_{ni}|^2$.

Application Interaction with classical EM waves

In general $$H = \frac{\left(\vec{P} - \frac{e}{c}\vec{A}\right)^2}{2m} + eV(\vec{R})$$ for an electron

in the presence of a classical $\vec{E}, \vec{B}$ field described by potentials $\vec{A}$, V with

$$\vec{B} = \vec{\nabla}\times\vec{A} \qquad \vec{E} = -\vec{\nabla}V - \frac{1}{c}\frac{\partial\vec{A}}{\partial t}$$

Use Coulomb gauge to describe EM waves.

This means: $$\vec{\nabla}\cdot\vec{A} = 0$$
$$V(\vec{R}) = 0.$$

So $$\vec{A} = 2A_0\,\hat{n}\cos\left(\frac{\omega}{c}\hat{k}\cdot\vec{R} - \omega t\right)$$

ω = angular frequency

$\hat{n}\cdot\hat{k} = 0$

$\hat{n}\cdot\hat{n} = 1$

$\hat{k}\cdot\hat{k} = 1$

$\hat{n}$: polarization vector (book calls it $\hat{\varepsilon}$)

$\hat{k}$: wavevector (book calls it $\hat{n}$).

Then $$H = \frac{P^2}{2m_e} - \frac{e}{m_e c}\vec{A}\cdot\vec{P} + V_{other}$$ (neglect A^2 as small).

A note on units: Sakurai (like most QM books) uses gaussian units. Some other books use MKS = SI units (Griffiths, for example).

Key EM formulas in gaussian units:

$\vec{\nabla}\cdot\vec{E} = 4\pi\rho$ (SI: ρ/ϵ_0)

$\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t}$ (SI: $-\partial\vec{B}/\partial t$)

$\vec{\nabla}\cdot\vec{B} = 0$ (SI: 0)

$\vec{\nabla}\times\vec{B} = \frac{4\pi}{c}\vec{J} + \frac{1}{c}\frac{\partial\vec{E}}{\partial t}$ (SI: $\mu_0\vec{J} + \frac{1}{c^2}\frac{\partial\vec{E}}{\partial t}$).

$U_{EM} = \frac{1}{8\pi}(E^2+B^2)$ (SI: $\frac{\epsilon_0}{2}E^2 + \frac{B^2}{2\mu_0}$) $\left(\frac{\text{energy}}{\text{volume}}\right)$

Take $H_0 = \frac{p^2}{2m_e} + V_{other}$ binding potential of atom, etc. not from EM wave

$$V(t) = -\frac{e}{m_e c}A_0\,\hat{n}\cdot\vec{P}\left[e^{i(\frac{\omega}{c}\hat{k}\cdot\vec{R})}e^{-i\omega t} + e^{-i(\frac{\omega}{c}\hat{k}\cdot\vec{R})}e^{i\omega t}\right]$$

$$H = H_0 + V(t).$$

This is a harmonic perturbation.

"Stimulated emission" and "absorption" refer to particle emitting or absorbing EM waves with frequency ω.

What is the energy flux of these waves?

$$\vec{A} = \mathrm{Re}\left[2A_0\,\hat{n}\,e^{i(\frac{\omega}{c}\hat{k}\cdot\vec{R}-\omega t)}\right]$$

So

$$\vec{B} = \vec{\nabla}\times\vec{A} = \mathrm{Re}\left[2A_0\,\frac{i\omega}{c}(\hat{k}\times\hat{n})\,e^{i(\frac{\omega}{c}\hat{k}\cdot\vec{R}-\omega t)}\right]$$

$$\vec{E} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t} = \mathrm{Re}\left[2A_0\frac{i\omega}{c}\,\hat{n}\,e^{i(\frac{\omega}{c}\hat{k}\cdot\vec{R}-\omega t)}\right]$$

Then $\langle B^2\rangle = \langle E^2\rangle = 4A_0^2\frac{\omega^2}{c^2}\langle\sin^2(\ldots)\rangle = 2A_0^2\frac{\omega^2}{c^2}$

$\langle\ \rangle$ means time-average here!

So, the time-averaged energy density is

$$\langle u_{EM} \rangle = \frac{1}{8\pi}\left(4 A_0^2 \frac{\omega^2}{c^2}\right) = \frac{A_0^2 \omega^2}{2\pi c^2}.$$

Then energy flux, $\left(\frac{\text{energy}}{(\text{time})(\text{area})}\right)$, is therefore

$$\boxed{c\, u_{EM} = \frac{A_0^2 \omega^2}{2\pi c}.}$$

Now, back to the absorption rate:

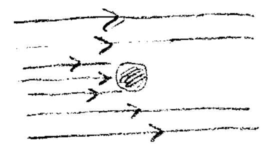
$$W_{i \to n} = \frac{2\pi}{\hbar} \frac{e^2}{m_e^2 c^2} A_0^2 \left| \langle n | e^{i \frac{\omega}{c} \hat{k} \cdot \vec{R}} \hat{n} \cdot \vec{P} | i \rangle \right|^2 \delta(E_n - E_i - \hbar\omega).$$

Note this is proportional to A_0^2, or the energy flux.

Define the <u>absorption cross-section</u>:

$$\sigma_{abs} \equiv \frac{\left[\frac{(\text{energy})}{(\text{time})} \text{ absorbed by atom } (i \to n)\right]}{\left[\text{energy flux} = \frac{\text{energy}}{(\text{time})(\text{area})} \text{ of light}\right]}$$

has units of <u>area</u>



$$= \frac{\begin{pmatrix}\text{energy absorbed} \\ \text{in each } i \to n \\ \text{process}\end{pmatrix} (\text{rate for } i \to n)}{c\, u_{EM}}$$

$$= \frac{(\hbar\omega)\left[\frac{2\pi}{\hbar}\left(\frac{e^2}{m^2 c^2}\right) A_0^2 \left| \langle n | e^{i\left(\frac{\omega}{c}\hat{k}\cdot\vec{R}\right)} \hat{n}\cdot\vec{P} | i \rangle \right|^2 \delta(E_n - E_i - \hbar\omega)\right]}{\left(\frac{A_0^2 \omega^2}{2\pi c}\right)}$$

$$\boxed{\sigma_{abs} = \frac{4\pi^2 \hbar}{m_e^2 \omega} \alpha \left| \langle n | e^{i\left(\frac{\omega}{c}\hat{k}\cdot\vec{R}\right)} \hat{n}\cdot\vec{P} | i \rangle \right|^2 \delta(E_n - E_i - \hbar\omega)}$$

This should be integrated over continuous states $|n\rangle$ (ionization) or discrete states $|n\rangle$ (excitation) with $E_n \simeq E_i + \hbar\omega$ — energy of absorbed photon.

Discrete states $|n\rangle$ may be closely spaced, or slightly broadened due to finite lifetime.

$$\delta(E_n - E_i - \hbar\omega) \to \frac{\hbar\gamma}{2\pi} \frac{1}{\left[(E_n - E_i)^2 + \hbar^2\gamma^2/4\right]}$$

$\gamma = 1/\text{lifetime}$ of excited state.

Electric Dipole Approximation

Assume wavelength of light $\lambda \gg$ size of atom $R_{atom} \approx \frac{a_0}{Z_{eff}}$.

For a light atom (or a K-shell electron) with $Z_{eff} \approx Z$,

$$\underset{\substack{\Uparrow \\ \text{photon} \\ \text{energy}}}{\hbar\omega} \sim \underset{\substack{\Uparrow \\ \text{atomic} \\ \text{energy} \\ \text{levels}}}{\Delta E_{atom}} \sim \frac{Z^2 e^2}{a_0} \sim \frac{Ze^2}{R_{atom}}$$

So $\lambda\!\!\!^{-} \equiv \frac{\lambda}{2\pi} = \frac{c}{\omega} \sim \frac{c\hbar R_{atom}}{Z e^2} \sim \frac{R_{atom}}{Z\alpha} \sim \left(\frac{137}{Z}\right) R_{atom}$

Therefore, $\frac{\lambda\!\!\!^{-}}{R_{atom}} \sim \left(\frac{137}{Z}\right) \gg 1$ if Z is small. ✓

Now $e^{i\left(\frac{\omega}{c}\hat{k}\cdot\vec{R}\right)} = 1 + i\frac{\vec{R}}{\lambda\!\!\!^{-}}\cdot\hat{k} + \left(\frac{i\vec{R}}{\lambda\!\!\!^{-}}\cdot\hat{k}\right)^2 + \ldots$

Since $\langle\vec{R}\rangle \sim R_{atom}$, each term is $\ll 1$.

So: $\langle n| e^{i\left(\frac{\omega}{c}\hat{k}\cdot\vec{R}\right)}\hat{n}\cdot\vec{P}|i\rangle \approx \hat{n}\cdot\langle n|\vec{P}|i\rangle$

Suppose $\hat{k} = \hat{z}$, $\hat{n} = \hat{x}$ = polarization direction.

Then $\langle\;\rangle = \langle n|P_x|i\rangle$

Trick: $P_x = \frac{m}{i\hbar}[X, H_0]$ (since $H_0 = \frac{P^2}{2m} + V(\vec{R})$ and $[X, P_x] = +i\hbar$

So $\langle n|P_x|i\rangle = \frac{m}{i\hbar}\langle n|[X,H_0]|i\rangle = im\omega_{ni}\,\langle n|X|i\rangle$.

↖ dipole operator

So $\boxed{\sigma_{abs} = 4\pi^2\alpha\,\omega_{ni}\,|\langle n|X|i\rangle|^2\,\delta(\omega-\omega_{ni})}$

More generally, replace X by coordinate along polarization of light.

Have used $\delta(E_n - E_i - \hbar\omega) = \frac{1}{\hbar}\delta(\omega-\omega_{ni})$.

<u>Selection rule</u>: Dipole absorption requires $|n\rangle$ and $|i\rangle$ to satisfy $\langle n|\vec{R}|i\rangle \neq 0$. (We'll return to this later...)

Consider excitation of the ground state $|i\rangle$.

Compute the quantity:

$$\int_0^\infty \sigma_{abs}(\omega)\, d\omega = \underbrace{\sum_n}_{\text{all excited states}} 4\pi^2 \alpha\, \omega_{ni} |\langle n|x|i\rangle|^2 \qquad \text{(δ-fn picks out contributions)}$$

Define $f_{ni} = \frac{2m\omega_{ni}}{\hbar} |\langle n|x|i\rangle|^2$ = oscillator strength.

PHYS 660, HW set 5, problem #2 (Sakurai #5 on page 144) says:

$$\sum_n f_{ni} = 1 \qquad \text{(Thomas - Reiche - Kuhn sum rule).}$$

So $$\int_0^\infty \sigma_{abs}(\omega)\, d\omega = \sum_n 4\pi^2 \alpha \left(\frac{\hbar}{2m}\right) f_{ni} = \frac{2\pi^2 \alpha \hbar}{m} = \frac{2\pi^2}{m}\left(\frac{e^2}{\hbar c}\right)\hbar$$

$$= \frac{2\pi^2 e^2}{m_e c}$$

This reproduces a classical sum rule (no $\hbar$).

Can also be derived with a classical treatment.

Stimulated Emission of Light

Now consider the case $E_i = E_n + \hbar\omega$.
So the state $|i\rangle$ goes to a lower state $|n\rangle$, emitting a photon with energy $\hbar\omega$.

As we saw, the formula for the rate is the same, but with $\delta(E_n - E_i + \hbar\omega)$ instead of $\delta(E_n - E_i - \hbar\omega)$:

$$w_{i\to n} = \frac{2\pi}{\hbar} \frac{e^2}{m^2 c^2} A_0^2 \, |\langle n| e^{i(\frac{\omega}{c}\hat{k}\cdot\vec{R})} \hat{n}\cdot\vec{P}|i\rangle|^2 \, \delta(E_n - E_i + \hbar\omega)$$

Note this emission rate is proportional to the intensity of radiation already present (A_0^2).

Also, note $W_{i\to n}^{\text{absorption}} = W_{n\to i}^{\text{emission}}$.

rates per unit energy, E_n and E_i, respectively.