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Quantum Mechanics 3 Homework 7

1) **Obtain $\langle n|U(0,-\infty)|n\rangle$ in second order in H_I. Extract the terms proportional to $\frac{1}{\varepsilon^2}$ and $\frac{1}{\varepsilon}$ in the limit $\varepsilon \to 0$. Compare your result with an expression of the form $e^{-\frac{i}{\hbar}\Delta\varepsilon_n T} e^{-\frac{\Gamma_n}{2}T}$ with $T = \frac{1}{\varepsilon}$ and $\Delta\varepsilon_n$ and Γ_n the energy shift and decay rate, respectively.**

Recall that

$$\Gamma_n = \frac{2\pi}{\hbar}\sum_{m\neq n}\left|\langle m|H_I|n\rangle\right|^2 \delta(E_m - E_n)$$

and

$$\Delta\varepsilon_n = \langle n|H_I|n\rangle + \lim_{\eta\to 0}\sum_{m\neq n}\frac{\left|\langle n|H_I|m\rangle\right|^2}{E_n - E_m + i\eta}$$

The perturbed state is given by:

$$|\tilde{n}\rangle = U(0,-\infty)|n\rangle = |n\rangle - \frac{i}{\hbar}\int_{-\infty}^{0} dt' H_I(t')|n\rangle - \frac{1}{2\hbar^2}\int_{-\infty}^{0}\int_{-\infty}^{0} dt'dt''\left(H_I(t')H_I(t'')\theta(t'-t'') + H_I(t'')H_I(t')\theta(t''-t')\right)|n\rangle + \ldots$$

Strategically inserting $I = \sum_m |m\rangle\langle m|$ and applying $\langle n|$ I may obtain in the second order:

$$\langle n|\tilde{n}\rangle = 1 - \frac{i}{\hbar}\int_{-\infty}^{0} dt'\langle n|H_I(t')|n\rangle$$

$$+\frac{1}{2\hbar^2}\sum_m \int_{-\infty}^{0}\int_{-\infty}^{0} dt'dt''\left(\langle n|H_I(t')|m\rangle\langle m|H_I(t'')\theta(t'-t'') + \langle n|H_I(t'')|m\rangle\langle m|H_I(t')\theta(t''-t')\right)|n\rangle$$

Now recalling the form of my interaction Hamiltonian,

$$\langle m|H_I(t)|n\rangle = \langle m|H_I|n\rangle e^{\frac{i}{\hbar}(E_m - E_n)t} e^{\varepsilon t}$$

Above, $\langle m|H_I|n\rangle$ is now time-independent.

Then I have:

$$\langle n|\tilde{n}\rangle = 1 - \frac{i}{\hbar}\langle n|H_I|n\rangle \int_{-\infty}^{0} dt' e^{\varepsilon t}$$

$$-\sum_m \frac{\left|\langle n|H_I|m\rangle\right|^2}{\hbar^2} \int_{-\infty}^{0}\int_{-\infty}^{0} dt' dt'' \left(e^{\frac{i}{\hbar}(E_n - E_m)(t'-t'')} e^{\varepsilon t'} e^{\varepsilon t''} \theta(t'-t'') + e^{-\frac{i}{\hbar}(E_n - E_m)(t'-t'')} e^{\varepsilon t'} e^{\varepsilon t''} \theta(t''-t') \right)$$

Integrating, I see that in this case, the two terms in the second-order integral give the same result.

$$\langle n|\tilde{n}\rangle = 1 - \frac{i}{\hbar}\frac{\langle n|H_I|n\rangle}{\varepsilon} e^{\varepsilon t} - \sum_m \frac{\left|\langle n|H_I|m\rangle\right|^2}{\hbar^2} \int_{-\infty}^{0} dt \left(\frac{e^{2t\varepsilon}\theta(-t) + e^{\frac{i}{\hbar}(E_n - E_m)t} e^{t\varepsilon}\theta(t)}{-\frac{i}{\hbar}(E_n - E_m) + \varepsilon} \right)$$

Integrating what remains, I have:

$$\langle n|\tilde{n}\rangle = 1 - \frac{i\langle n|H_I|n\rangle}{\hbar\varepsilon} e^{\varepsilon t} - \frac{1}{2\hbar^2}\sum_m \frac{\left|\langle n|H_I|m\rangle\right|^2}{\varepsilon\left(-\frac{i}{\hbar}(E_n - E_m) + \varepsilon\right)}$$

Now all that's left to do is take the limit as $\varepsilon \to 0$, and separate the sum over m into a separate sum for degenerate, identity, and non-degenerate cases (note that except for the $n = m$ case, there are 2 of each term):

$$\langle n|\tilde{n}\rangle = 1 - \frac{i}{\hbar\varepsilon}\langle n|H_I|n\rangle - \frac{i}{\hbar\varepsilon}\sum_{m\neq n, E_n \neq E_m} \frac{\left|\langle n|H_I|m\rangle\right|^2}{(E_n - E_m)} - \frac{1}{2\hbar^2\varepsilon^2}\left|\langle n|H_I|n\rangle\right|^2 - \frac{\pi}{\hbar\varepsilon^2}\sum_{m\neq n, E_n = E_m}\left|\langle n|H_I|m\rangle\right|^2$$

Identifying terms, then, I have:

$$\langle n|\tilde{n}\rangle = 1 - \frac{i}{\hbar}T\Delta E_n^{(1)} - \frac{i}{\hbar}T\Delta E_n^{(2)} + \frac{1}{2}\left(-\frac{i}{\hbar}\right)^2 T^2\left(\Delta E_n^{(1)}\right)^2 - \frac{\Gamma_n}{2}$$

So, then, I see that these represent several terms from $e^{-\frac{i}{\hbar}\Delta\varepsilon_n T} e^{-\frac{\Gamma_n}{2}T}$; namely, if I let:

$$\Delta\varepsilon_n = \Delta E_n^{(1)} + \Delta E_n^{(2)} + \ldots$$

Then the procedure that I followed gives me all terms of the product of these expansions out to terms square in H_I :

$$e^{-\frac{i}{\hbar}\Delta\varepsilon_n T} e^{-\frac{\Gamma_n}{2}T} = \left(1 + \left(-\frac{i}{\hbar}\Delta\varepsilon_n\right)T + \frac{1}{2}\left(-\frac{i}{\hbar}\Delta\varepsilon_n\right)^2 T^2 + \ldots\right)\left(1 - \frac{\Gamma_n}{2}T + \ldots\right)$$

2) **Consider hydrogenic atoms in a cavity in which a photon bath is in equilibrium at temperature T and consider transitions only between ground and first excited states (only two levels: A, B).**

a) **Follow the steps in class and obtain Γ_{abs} and Γ_{em}. Leave the angular integral $\sum_\lambda \int \frac{d\Omega}{4\pi} \vec{e}_\lambda \cdot \vec{x}_{AB}$ unspecified.**

$$H_I^{abs} = \frac{1}{\sqrt{V}}\left(-\frac{e}{mc}\right) c_B^+ c_A a_{k,\lambda} \int d^3x U_B^*(\vec{x}) \vec{A}(\vec{x}) \cdot \hat{\vec{p}} U_A(\vec{x})$$

$$H_I^{em} = \frac{1}{\sqrt{V}}\left(-\frac{e}{mc}\right) c_B c_A^+ a_{k,\lambda}^+ \int d^3x U_A^*(\vec{x}) \vec{A}(\vec{x}) \cdot \hat{\vec{p}} U_B(\vec{x})$$

$$\hat{\vec{p}} = -i\hbar\vec{\nabla}_x$$

$$\vec{A}(\vec{x}) = \sum_{k,\lambda} \sqrt{\frac{\hbar c^2}{2\omega(\vec{k})}} \vec{\varepsilon}_\lambda(\vec{k}) e^{i\vec{k}\cdot\vec{x}} \rightarrow dipole \quad approximation \rightarrow \sum_{k,\lambda} \sqrt{\frac{\hbar c^2}{2\omega(\vec{k})}} \vec{\varepsilon}_\lambda(\vec{k})$$

Further, Fermi's Golden Rule says that $\Gamma_x = \frac{2\pi}{\hbar} \sum_f \left|\langle F|H_I^x|I\rangle\right|^2 \delta(\varepsilon_f - \varepsilon_i)$

I will do absorption first: I seek to use Fermi's Golden Rule to obtain a lifetime.
$|F\rangle = |B\rangle|n_{k,\lambda} - 1\rangle \quad |I\rangle = |A\rangle|n_{k,\lambda}\rangle$

Now I see that

$$\langle F|H_I^{abs}|I\rangle = \frac{1}{\sqrt{V}} \langle B|c_B^+ c_A|A\rangle \langle n_{k,\lambda} - 1|a_{k,\lambda}|n_{k,\lambda}\rangle \left(-\frac{e}{mc}\right) \sqrt{\frac{\hbar c^2}{2\omega(\vec{k})}} \int d^3x U_B^*(\vec{x}) \vec{e}_\lambda(\vec{k}) \cdot \hat{\vec{p}} U_A(\vec{x})$$

However, I notice that

$$\int d^3x U_B^*(\vec{x}) \hat{\vec{p}} U_A(\vec{x}) = -\frac{im}{\hbar} \int d^3x U_B^*(\vec{x}) \left[\vec{x}, H_0^m\right] U_A(\vec{x}) = \frac{im}{\hbar} \langle B|\hat{\vec{x}}|A\rangle (E_B - E_A)$$

$$\langle n_{k,\lambda} - 1|a_{k,\lambda}|n_{k,\lambda}\rangle = \sqrt{n_{k,\lambda}}$$

$$\langle B|c_B^+ c_A|A\rangle = 1$$

and so:

$$\langle F|H_I^{abs}|I\rangle = \frac{1}{\sqrt{V}} \frac{im}{\hbar} (E_B - E_A) \sqrt{n_{k,\lambda}} \left(-\frac{e}{mc}\right) \sqrt{\frac{\hbar c^2}{2\omega(\vec{k})}} \vec{e}_\lambda(\vec{k}) \cdot \langle B|\hat{\vec{x}}|A\rangle$$

Then, using $\hbar\omega(k) = \hbar ck = E_B - E_A$, I see that:

$$\left|\langle F|H_I^{abs}|I\rangle\right|^2 = \frac{e^2}{2V}(E_B - E_A)n_{k,\lambda}\left|\vec{e}_\lambda(\vec{k})\cdot\langle B|\hat{\vec{x}}|A\rangle\right|^2$$

Now in Fermi's Golden Rule,

$$\Gamma_{abs} = \frac{2\pi}{\hbar}\sum_f \frac{e^2}{2V}(E_B - E_A)n_{k,\lambda}\left|\vec{e}_\lambda(\vec{k})\cdot\langle B|\hat{\vec{x}}|A\rangle\right|^2 \delta(E_B - E_A - \hbar ck)$$

$$\sum_f \rightarrow \sum_{k,\lambda} \quad \frac{1}{V}\sum_{k,\lambda} \rightarrow \sum_\lambda \int \frac{d^3k}{(2\pi)^3} = \sum_\lambda \int_0^\infty k^2 dk \int \frac{d\Omega}{8\pi^3}$$

$$\Gamma_{abs} = \frac{\pi e^2}{\hbar}(E_B - E_A)n_{k,\lambda}\sum_\lambda \int_0^\infty k^2 \delta(E_B - E_A - \hbar ck)dk \int \frac{d\Omega}{8\pi^3}\left|\vec{e}_\lambda(\vec{k})\cdot\langle B|\hat{\vec{x}}|A\rangle\right|^2$$

$$\int_0^\infty k^2 \delta(E_B - E_A - \hbar ck)dk = \frac{(E_B - E_A)^2}{(\hbar c)^3}$$

$$\Gamma_{abs} = \frac{e^2}{2\hbar}\frac{(E_B - E_A)^3}{(\hbar c)^3} n_{k,\lambda}\sum_\lambda \int \frac{d\Omega}{4\pi^2}\left|\vec{e}_\lambda(\vec{k})\cdot\langle B|\hat{\vec{x}}|A\rangle\right|^2$$

where now $\vec{k} = \frac{(E_B - E_A)}{\hbar c}\hat{n}$.

Emission is very similar; summarizing, the only real differences are:

$$\langle F|H_I^{em}|I\rangle = \frac{1}{\sqrt{V}}\langle A|c_A^+ c_B|B\rangle\langle n_{k,\lambda}+1|a^+{}_{k,\lambda}|n_{k,\lambda}\rangle\left(-\frac{e}{mc}\right)\sqrt{\frac{\hbar c^2}{2\omega(\vec{k})}}\int d^3x U_A^*(\vec{x})\vec{e}_\lambda(\vec{k})\cdot\hat{\vec{p}}U_B(\vec{x})$$

$$\langle n_{k,\lambda}+1|a^+{}_{k,\lambda}|n_{k,\lambda}\rangle = \sqrt{n_{k,\lambda}+1}$$

Propagating these through (square-roots and absolute values ensure that that the sign remains the same:

$$\Gamma_{em} = \frac{e^2}{2\hbar}\frac{(E_B - E_A)^3}{(\hbar c)^3}(1 + n_{k,\lambda})\sum_\lambda \int \frac{d\Omega}{4\pi^2}\left|\vec{e}_\lambda(\vec{k})\cdot\langle B|\hat{\vec{x}}|A\rangle\right|^2$$

b) Approximate the angular integral by the Bohr radius of a hydrogenic atom and estimate Γ_{abs} , Γ_{em} for 300K and 3000K.

For emission, I see that *within factors that I had to add to make units work*, stimulated emission was very unlikely.

$$\int \frac{d\Omega}{4\pi^2} \left| \vec{e}_\lambda \left(\vec{k}\right) \cdot \langle B | \dot{\vec{x}} | A \rangle \right|^2 \rightarrow a_0^2$$

$$\Gamma_{em} \rightarrow \left(1 + n_{k,\lambda}\right) \frac{e^2}{\hbar c} \left(\frac{\Delta E}{\hbar}\right)^3 \left(\frac{a_0}{c}\right)^2 = \left(1 + n_{k,\lambda}\right) \frac{e^2}{\hbar c} \left(\frac{\Delta E}{\hbar}\right)^3 \left(\frac{a_0}{c}\right)^2$$

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$$

$$\Delta E = \frac{3}{4}(13.6)eV$$

$$a_0 = 52.9 \cdot 10^{-3} nm$$

$$\hbar c = 197.3 eV \cdot nm$$

$$\hbar = 6.582 \cdot 10^{-16} eV \cdot s$$

$$\Gamma_{em} \rightarrow \left(1 + n_{k,\lambda}\right) \frac{e^2}{\hbar c} \left(\frac{\Delta E}{\hbar}\right)^3 \left(\frac{a_0}{c}\right)^2 = \left(1 + n_{k,\lambda}\right) \left[8.46 \cdot 10^8 s^{-1}\right]$$

Using the value for number of particles from the Canonical ensemble:

$$k_B = 8.67 \cdot 10^{-5} \frac{eV}{K}$$

$$n_{k,\lambda} = \frac{e^{-\frac{117647}{T}}}{e^{-\frac{117647}{T}} + 1}$$

$$\Gamma_{em}(300K) \approx 1.69 \cdot 10^9 s^{-1}$$

$$\Gamma_{em}(3000K) \approx 1.69 \cdot 10^9 s^{-1}$$

So I see that the emissive lifetime is on the nanosecond scale, across temperatures. The absorption formula is practically identical, except for the factor arising from spontaneous emission:

$$\Gamma_{abs}(300K) \approx 8.46 \cdot 10^8 s^{-1}$$

$$\Gamma_{abs}(3000K) \approx 8.46 \cdot 10^8 s^{-1}$$

So I see that the expected lifetime of the non-excited state is also very low: the particles rapidly exchange energy.

c) In the same approximation, estimate the radiative lifetime $\tau = \frac{1}{\Gamma_{em}}$ **at** $T = 0$ **for the excited state.**

In this approximation, $n_{k,\lambda} \to 0$ and so

$$\Gamma_{em} \to \left(1+n_{k,\lambda}\right)\frac{e^2}{\hbar c}\left(\frac{\Delta E}{\hbar}\right)^3\left(\frac{a_0}{c}\right)^2 = \left(1+n_{k,\lambda}\right)\left[8.46\cdot 10^8 s^{-1}\right]$$
$$\tau \to 1.18\cdot 10^{-9} s$$

or about a nanosecond.

3) **Consider N atoms with only two levels A and B in a cavity with blackbody radiation in equilibrium at temperature T.**

a) **If at time $t=0$ all the atoms are prepared to be in the level A, give the populations $N_A(t)$, $N_B(t)$ and show that they approach their equilibrium value exponentially.**

The atoms in the cavity will change population through gain and loss: namely,

$$\frac{dN_A}{dt} = N_B\Gamma_{em} - N_A\Gamma_{abs} \qquad \frac{dN_B}{dt} = N_A\Gamma_{abs} - N_B\Gamma_{em}$$

However, since any atom must be in state A or B,

$$\frac{d\left(N_A+N_B\right)}{dt} = 0$$

then in equilibrium:

$$\left.\frac{dN_A}{dt}\right|_{eq} = 0$$

or

$$\left.\frac{dN_A}{dt}\right|_{eq} = 0 = N_{B,eq}\Gamma_{em} - N_{A,eq}\Gamma_{abs}$$
$$\frac{N_{B,eq}}{N_{A,eq}} = \frac{\Gamma_{abs}}{\Gamma_{em}}$$

$$\frac{dN_A}{dt} = \left(N - N_A\right)\Gamma_{em}$$

This implies that the function N_A must approach its equilibrium exponentially. Clearly, a similar proof can be given for N_B.

b) What are the equilibrium values $N_{A,eq} = N_A(\infty)$, $N_{B,eq} = N_B(\infty)$ in terms of N, Γ_{abs}, Γ_{em}?

There are certainly always N particles. From part (a), I found that

$$\frac{N_{B,eq}}{N_{A,eq}} = \frac{\Gamma_{abs}}{\Gamma_{em}}$$

Then,

$$\frac{N_{A,eq}}{N - N_{A,eq}} = \frac{\Gamma_{em}}{\Gamma_{abs}}$$

$$N_{A,eq} = N\frac{\frac{\Gamma_{em}}{\Gamma_{abs}}}{1+\frac{\Gamma_{em}}{\Gamma_{abs}}} \quad N_{B,eq} = N\frac{1}{1+\frac{\Gamma_{em}}{\Gamma_{abs}}}$$

c) Consider these to be hydrogenic atoms with only ground and first excited states A, B and assume that the angular average $\sum_\lambda \int \frac{d\Omega}{4\pi} \vec{e}_\lambda \cdot \vec{x}_{AB}$ is approximately the Bohr radius. Estimate the equilibrium time scale τ_{eq} for $T = 300K, 3000K$, where τ_{eq} is defined from the exponential approach to the equilibrium of the populations $\propto e^{-\frac{t}{\tau_{eq}}}$. τ_{eq} is solely a function of $\Gamma_{em}, \Gamma_{abs}$.

Using

$$\frac{dN_A}{dt} = (N - N_A)\Gamma_{em} - N_A\Gamma_{abs}$$

$$\frac{dN_A}{dt} = N\Gamma_{em} - (\Gamma_{em} + \Gamma_{abs})N_A(-N_A) - N_A\Gamma_{abs}$$

Solving this under the initial condition $N_A(0) = N$, I have:

$$N_A = \frac{\Gamma_{abs}e^{(-\Gamma_{abs}-\Gamma_{em})t} + \Gamma_{em}}{\Gamma_{abs} + \Gamma_{em}}N$$

The equilibrium timescale should then be like $\frac{1}{\Gamma_{abs} + \Gamma_{em}}$: Taking the results from 2b, I have:

$$\frac{1}{\Gamma_{abs}+\Gamma_{em}}=\frac{1}{1.69\cdot 10^{9}+8.46\cdot 10^{8}}\,s=3.94\cdot 10^{-10}\,s$$

This is practically independent of temperature, since the lifetimes of these states were identical within the proper number of significant figures.