ISSN: 2525-6599
REVISTA UNIFEV:
Ciência & Tecnologia

TRANSITION BETWEEN ATOMIC STATES AND SEMI-CLASSICAL RADIATION THEORY USING QUANTUM PERTURBATION

MELO, Michael[1]

PULICI, Angelo Rober[2]

ABSTRACT

Some phenomena cannot be solved using the exact solution of the Schrödinger equation. However, using approximated methods such as perturbation theory we are able to obtain remarkable results considering terms up to second order. The physical phenomena studied here are the absorption and stimulated emission by the classical feature. In addition, we are going to discuss the physical meaning of perturbation theory when we treat the behaviour how initial state ket evolves as time goes on. We will evaluate the transition of probability between states, the rate and the energy involved in the atomic transitions. It will be introduced fundamental concepts of quantum mechanics, such as interaction picture, and a general perturbation theory using constant and sinusoidal time-dependent perturbation term. Concerning to these phenomena, we considered the perturbed term of the Hamiltonian of the interaction between the vector potential and electron momentum.

Keywords: Quantum Mechanics. Perturbation Theory. Photoelectric Effect.

INTRODUCTION

In the state-of-the-art of scientific knowledge, quantum mechanics is the last great theory that describes satisfactory the natural phenomena in a very small scale (COHEN-TANNOUGJI, et al., 1977)]. In this work, the concepts of quantum mechanics will be carried on in order to describe some phenomena of classical radiation interaction with matter. Moreover, to describe such phenomena, it is required to advance further with approximation methods, such as time-dependent perturbation

---

[1] Michael Melo is Bachelor in Physics for USP, with master in Civil Engineering for UNESP and PhD in Materials Science at UNESP at Applied Physics. Currently is professor at Centro Educacional de Votuporanga-Unifev. E-mail: michaeldemelo@hotmail.com

[2] Angelo Rober Pulici is Bachalor in Physics by Makenzie and is master in Molecular Biophysics at UNESP. Also is professor at Centro Educacional de Votuporanga – Unifev.

theory. Basic quantum concepts of perturbation theory will be described using the time-dependent potential and interaction picture. The two-state level problem is described in detail using the exact solution of Schrödinger equation. Concerning about the time-dependent perturbation theory, which the most problems faced in nature have no exact solution, we will apply the approximation method to solve absorption and stimulated emission. It is worthy to notice that the phenomena such as the photoelectric effect and the energy shift and decay width can be explained using quantum perturbation theory.

DEVELOPMENT

1 TIME-DEPENDENT POTENTIALS

In contrast with the quantum static, in which the potential is time-independent, many problems in nature of importance considerably hold potential that are dependent of time. Generally, the Hamiltonian can be partitioned in two terms; one containing time explicitly as follows $\hat{\mathrm{H}} = \hat{\mathrm{H}}_0 + \hat{\mathrm{V}}(t)$[1] If we consider the system initially populated at one of eigenstates of the Hamiltonian, for instance $|i\rangle$, the system will develop and, due to time-dependent potential, can undergo transitions to states other than $|i\rangle$, i.e., $n \neq i$. In this way, suppose that the physical system is, at $t = 0$, in an arbitrary state, in which can be described as a superposition of eigenkets of the Hamiltonian, such as

$$|\varphi; t = 0\rangle = |\varphi\rangle = \sum\nolimits_n c_n(0)\,|n\rangle. \qquad (1)^1$$

With the progress of time, the physical state develops and its dynamic is described by time evolution operator (Sakurai, 1994). Applying this temporal operator in Equation (1) and using the Schrödinger equation for the stationary case, we get

$$|\varphi; t\rangle = \sum\nolimits_n c_n(t)\, e^{-\frac{i}{\hbar}\mathrm{E}_n t}|n\rangle. \qquad (2)^2$$

---

[1] It is important to notice that at $t = 0$, in the Schrödinger picture, the basis kets does not change as time evolves. Thus, in order to investigate the dynamic of physical state, the calculation of coefficients it substantially important for this work.

[2] The time evolution operator in the Schrödinger picture is given by $\mathbf{U}(t) = e^{-\frac{i}{\hbar}\mathbf{H}t}$, where $\hbar$ is the reduced Planck constant and $\mathbf{H}$ is the Hamiltonian of the physical system.

The time-evolution of the coefficients, as we can observe in the above equation, depends only on the time-dependent potential.[1] The probability of finding the system in an eigenstate $|n\rangle$ is proportional to $|c_n(t)|^2$. Clearly, we easily verify that the probability changes according to the value of the potential in the Hamiltonian.

2 THE INTERACTION PICTURE

To solve problems using the perturbation theory, it is required introduce another concept relevant and useful, which is the Interaction Picture.[2] The time evolution of a given state ket in the Schrödinger Picture was described in the Equation (2), in which will be represented by the subscript *S* for Schrödinger Picture and *I* for the Interaction Picture.

Defining $|\varphi, t_0; t\rangle_I = e^{i\mathbf{H}_0 t/\hbar}|\varphi, t_0; t\rangle_S$ as the change of the state described from one picture to another and multiplying $i\hbar\frac{\partial}{\partial t}$ taking use of the Schrödinger equation, we obtain

$$i\hbar\frac{\partial}{\partial t}|\varphi, t_0; t\rangle_I = \mathbf{V}_I|\varphi, t_0; t\rangle_I \tag{3}$$
[3]

Also, $\boldsymbol{V}_I$ stands for the potential and this equation is so-called Schrödinger-like equation in Interaction Picture. [4] Claiming for the Heisenberg-like equation in interaction picture, by which describes the dynamic of the observables, it is necessary to consider the change of basis of observables, between Schrödinger and Interaction Pictures obtained through the evaluation of the Equation (3), i.e.,

$$\boldsymbol{A}_I = e^{\frac{i\mathbf{H_0}t}{\hbar}}\,\boldsymbol{A}_S\, e^{\frac{-i\mathbf{H}_0 t}{\hbar}}. \tag{4}$$

Differentiating with respect to time, we obtain the Heisenberg-like equation

$$\dot{\mathbf{A}}_I = -\frac{i}{\hbar}[\mathbf{A}_I, \mathbf{H}_0] \tag{5}$$

---

[1] Even if the time-dependent potential is absent, the exponential term is present. This can assure that the evolution of the coefficients are exclusively dependent on the potential.

[2] To read more about Interaction Picture and the differences among others, such as Schrödinger and Heisenberg Picture, please, go to reference (SAKURAI, 1994).

[3] All quantum operators will be represented by bold characters instead of using a caret.

[4] This equation is quite similar to the Schrödinger equation in the Schrödinger Picture, but instead of $\mathbf{H}$, the equation replaced by $\mathbf{V}_I$, being so-called Schrödinger-like equation.

where we have used the $\dot{\mathbf{A}}_S = 0$ in Schrödinger picture. Describing a physical system by an arbitrary state ket in interaction picture, using the same energy eigenkets basis $|n\rangle$, follows

$$|\varphi, t_0 = 0; t\rangle_I = \sum_n c_n(t)\,|n\rangle. \tag{6}$$

The main idea is to determine the expansion coefficients of (6) in order to evaluate the probability of finding the physical system in any of the energy eigenstates $|n\rangle$. Using the Schrödinger-like equation obtained in Equation (3) and recognizing that $c_n(t) = \langle n|\varphi, t_0; t\rangle_I$, it follows

$$i\hbar\dot{c}_n(t) = \langle n|e^{i\mathbf{H}_0 t/\hbar}\,\mathbf{V}\,e^{-i\mathbf{H}_0 t/\hbar}\,|\varphi, t_0; t\rangle_I \tag{7}$$

where we have used Equation (4). Inserting the unit operator in Equation (7), we obtain

$$i\hbar\dot{c}_n(t) = \sum_m e^{i(\mathrm{E}_n - \mathrm{E}_m)t/\hbar}\langle n|\,\mathbf{V}\,|m\rangle\langle m|\varphi, t_0; t\rangle_I \tag{8}$$

Using the definition of characteristic angular frequency between two states, i.e., $\omega_{nm} = (\mathrm{E}_n - \mathrm{E}_m)/\hbar$, defining the matrix element $\langle n|\,V\,|m\rangle$ as V_{nm} and $c_m(t) = \langle m|\varphi, t_0; t\rangle_I$, we finally get

$$i\hbar\dot{c}_n(t) = \sum_m e^{i\omega_{nm}t}\mathbf{V}_{nm}c_m(t). \tag{9}$$

The Equation (9) is the coupled differential equation for the expansion coefficients. Therefore, to evaluate the probability of finding the physical system in any energy eigenstate is necessary to solve it.

3 TWO-SYSTEM PROBLEM

Most problems in nature cannot be solved with exact solutions, it is necessary to use approximation methods as perturbation that we are going to develop in this work. However, it is important and relevant described herein the two-system level problem in order to solve the differential equation obtained in Equation (9) for a given time-dependent potential. Consider a Hamiltonian and a time-dependent potential for such physical system as follows

$$\mathbf{H}_0 = \mathrm{E}_1|1\rangle\langle 1| + \mathrm{E}_2|2\rangle\langle 2| \tag{10}$$

$$\mathbf{V}(t) = \zeta\left(e^{i\omega t}|1\rangle\langle 2| + e^{-i\omega t}|2\rangle\langle 1|\right) \tag{11}$$

where we have that for $\zeta, \omega > 0$ and real. It is very clear to observe that time-dependent potential connects one state to another, undergoing a transition. The potential described before is purely off diagonal and it is possible to replace it in Equation (9). If the physical system is supposed to occupy initially the lower state, then the probability to find the system in the upper state is given by the Rabi's Formula[1] (PULICI, 2006),

$$|c_2(t)|^2 = (\zeta/\hbar)^2 \frac{1}{\Omega^2/4 + \zeta^2/\hbar^2} \sin^2\left(\sqrt{\Omega^2/4 + \zeta^2/\hbar^2}\, t\right). \tag{12}$$

The probability oscillates in time with an angular frequency $\widetilde{\Omega} = \sqrt{\Omega^2/4 + \zeta^2/\hbar^2}$, where $\Omega = \omega - \omega_{12}$. In the resonance condition[2] the amplitude oscillation is very large and, consequently, the probability in both of the states are

$$|c_2(t)|^2 = \sin^2(\zeta t/\hbar) \tag{13}$$

$$|c_1(t)|^2 = 1 - |c_2(t)|^2 = 1 - \sin^2\left(\frac{\zeta t}{\hbar}\right) = \cos^2\left(\frac{\zeta t}{\hbar}\right). \tag{14}$$

As we can notice, the system has all its energy entirely in the lower state. From 0 to $\pi\hbar/2\zeta$, the state $|1\rangle$ is gradually decreased and its excess of energy is given to the state $|2\rangle$, in a process so-called absorption. However, from $\pi\hbar/2\zeta$ to $\pi\hbar/\zeta$, the system undergoes a transition from state $|2\rangle$ to $|1\rangle$, in a process called emission, where the its excess of energy is emitted and the system restore its initial configuration. These processes of absorption and emission are due to the time-dependent potential and we can infer that this causes the transition between states. Though we are far away from the resonance condition, the system still experiences some transition between states. However, the amplitude of the oscillation decreases at half of its maximum when the angular frequency of the potential is

$$\omega = \omega_{12} \pm (2\zeta/\hbar). \tag{15}$$

Weaker the strength of the time-dependent potential applied in the physical system, narrow is the resonance peak of the transition.

4 TIME-DEPENDENT QUANTUM PERTURBATION THEORY

Whereas in the time-independent case the problem of solving the equation

---

[1] This formula has a great importance on atomic physics and the solution of the differential equation it is not demonstrated here.

[2] The resonance condition here is when the angular frequency of the time-dependent potential is near the angular frequency characteristic concerning the two states, i.e., $\omega \cong \omega_{12}$

$$i\hbar|\dot{n}\rangle = \mathbf{H}|n\rangle \tag{16}$$

is reduced to solve the eigenvalues of $\mathbf{H}$, the time-dependent case a frontal attempt on the full time-dependent Schrödinger equation becomes unavoidable (SHANKAR, 1994). Here, we are going to consider the perturbative solution to a class of phenomena as

$$\mathbf{H}(t) = \mathbf{H}^0 + \mathbf{H}^1(t) \tag{17}$$

where $\mathbf{H}^0$ is a time-independent part where the solution is known and $\mathbf{H}^1$ is the perturbation term. So far, we have described the transition of probabilities of finding the system in a specific energy eigenstate. For a general case, we must solve the coupled differential Equation (9) and expand its coefficients as perturbation terms. The coefficients $c_n(t)$ can be expanded as

$$c_n(t) = c_n^0 + c_n^1 + c_n^2 \cdots \tag{18}$$

where the terms of the right side are the related with the amplitudes of non-perturbed term, first-order, second-order, and so on. Initially the physical system is populated in a specific state $|i\rangle$ at $t = t_0$ and to apply the definition of the Interaction Picture for such case, it is convenient to choose a phase factor. Then, we have

$$|i, t_0; t_0\rangle_S = \mathbf{U}_S(t_0)|i\rangle = e^{-i\mathrm{E}_i t_0/\hbar}|i\rangle. \tag{19}$$

Doing the change of pictures, from Schrödinger to Interaction one, we get

$$|i, t_0; t_0\rangle_I = e^{i\mathbf{H}_0 t}|i, t_0; t_0\rangle_S = e^{-i(\mathrm{E}_i - \mathrm{E}_i)t/\hbar}|i\rangle = |i\rangle \rightarrow |i, t_0; t_0\rangle_I = |i\rangle_S. \tag{20}$$

At a later time, we must apply the time evolution operator in Equation (20). It becomes

$$|i, t_0; t\rangle_I = \mathbf{U}_I(t, t_0)|i, t_0; t_0\rangle_I = \mathbf{U}_I(t, t_0)|i\rangle. \tag{21}$$

The physical state $|i, t_0; t\rangle_I$ can be expanded in terms of energy eigenstates as

$$|i, t_0; t\rangle_I = \sum\nolimits_n c_n(t)\, |n\rangle. \tag{22}$$

Comparing (21) and (22), we have

$$\sum\nolimits_n c_n(t)\, |n\rangle = \mathbf{U}_I(t, t_0)|i\rangle. \tag{23}$$

From (23) we identify that

$$\langle m| \left(\sum\nolimits_n c_n(t)\right) |n\rangle = \langle m|\mathbf{U}_I(t, t_0)|i\rangle \Rightarrow c_n(t) = \langle n|\mathbf{U}_I(t, t_0)|i\rangle. \tag{24}$$

The expansion of the coefficients in Equation (9) means expand the transition amplitude of time evolution operator in Interaction Picture. Then, from the Schrödinger-like equation, we have that the evolution of a state ket in the Interaction Picture is given by

$$i\hbar\frac{\partial}{\partial t}\mathbf{U}_I(t,t_0)|i,t_0;t\rangle_I = \mathbf{H}_I^1(t)\mathbf{U}_I(t,t_0)|i\rangle \tag{25}$$[1]

$$i\hbar\frac{\partial}{\partial t}\mathbf{U}_I = \mathbf{H}_I^1(t)\mathbf{U}_I. \tag{26}$$

Integrating with respect to time,

$$\int_{t_0}^{t}\frac{\partial}{\partial t}\mathbf{U}_I(t',t_0)dt' = -\frac{i}{\hbar}\int_{t_0}^{t}\mathbf{H}_I^1(t')\mathbf{U}_I(t',t_0)\,dt' \tag{27}$$

And solving it, we get

$$\mathbf{U}_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t}\mathbf{H}_I^1(t')\mathbf{U}_I(t',t_0)\,dt'. \tag{28}$$

By iteration, we obtain the following approximated solution

$$\mathbf{U}_I(t,t_0) = 1 + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t}\mathbf{H}_I^1(t')dt' + \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}\mathbf{H}_I^1(t')dt'\int_{t_0}^{t'}\mathbf{H}_I^1(t'')\,dt'' + \cdots \tag{29}$$

where this equation is known as Dyson Series. Finally, all we need is replace this expansion in Equation (23) and find out the transition probabilities between energy states,

$$c_n(t) = \langle n|\left[1 + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t}\mathbf{H}_I^1(t')dt' + \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}\mathbf{H}_I^1(t')dt'\int_{t_0}^{t'}\mathbf{H}_I^1(t'')\,dt'' + \cdots\right]|i\rangle \tag{30}$$

Rearranging the terms and comparing with the expansion of the coefficients given in Equation (18)

$$c_n^{(0)} = \langle n|i\rangle = \delta_{n,i} \tag{31}$$

$$c_n^{(1)} = \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t}e^{i\omega_{ni}t'}\mathbf{H}_{ni}^1(t')dt' \tag{32}$$

$$c_n^{(2)} = \left(\frac{-i}{\hbar}\right)^2\sum_m\int_{t_0}^{t}\int_{t_0}^{t'}e^{i\omega_{nm}t'}\mathbf{H}_{nm}^1(t')e^{i\omega_{mi}t''}\mathbf{H}_{mi}^1(t'')\,dt'dt'' \tag{33}$$

---

[1] The time-dependent potential term was changed by a general perturbation term.

where $\mathbf{H}^1_{nm}$ are the matrix elements of the perturbed term of Hamiltonian in Interaction picture and $\omega_{ni} = (\mathrm{E}_n - \mathrm{E}_i)/\hbar$ is the characteristic angular frequency between two states of the transition. Finally, the transition of probability from one state $|i\rangle \rightarrow |n\rangle$ is given by

$$P_{i\rightarrow n}(t) = \left|c_n^{(1)} + c_n^{(2)} + \cdots\right|^2 \tag{34}$$

4.1 Constant Perturbation

Now we are able to deal with constant perturbation. Regard the perturbation term, we hold

$$\mathbf{H}^1(t) = \begin{cases} 0 & t < 0 \\ \mathbf{H}^1 & t \geq 0 \end{cases} \tag{35}$$

We can amend in Equation (35) in perturbation coefficients described in Equation(31-33), and then we have

$$c_n^{(0)} = \delta_{in} \tag{36}$$

$$c_n^{(1)} = \left(\frac{-i}{\hbar}\right) \mathbf{H}^1_{ni} \int_0^t e^{i\omega_{ni}t'} dt' \tag{37}$$

$$c_n^{(2)} = \left(\frac{-i}{\hbar}\right)^2 \sum\nolimits_m \mathbf{H}^1_{nm} \mathbf{H}^1_{mi} \int_0^t e^{i\omega_{nm}t'} dt' \int_0^{t'} e^{i\omega_{mi}t''}\, dt''. \tag{38}$$

At first, we are going to deal with the first-order term and we obtain after solving the integral in Equation (37)

$$c_n^{(1)} = \frac{\mathbf{H}^1_{ni}}{(\mathrm{E}_n - \mathrm{E}_i)} \left(1 - e^{i\omega_{ni}t}\right). \tag{39}$$

Therefore, the transition of the probability of first-order is given by

$$\left|c_n^{(1)}\right|^2 = \frac{4\left|\mathbf{H}^1_{ni}\right|^2}{(\mathrm{E}_n - \mathrm{E}_i)^2} \left[\sin^2\left(\frac{\omega_{ni}t}{2}\right)\right]. \tag{40}$$

We can observe that the probability of finding $|n\rangle$ depends not only on $|V_{ni}|^2$, but as well as on difference of energy between two states. Considering that we have many states with similar energy of final states $|n\rangle$, i.e., $E \sim E_n$, or $\omega \sim \omega_n$, and looking at the behaviour of this first-order transition of probability as a function of the angular frequency, we have

$$\left|c_n^{(1)}\right|^2 = \frac{4\left|\mathbf{H}_{ni}^1\right|^2}{\omega^2\hbar^2}[\sin^2(\omega t/2)] = \frac{\left|\mathbf{H}_{ni}^1\right|^2}{\hbar^2}\frac{4[\sin^2(\omega t/2)]}{\omega^2}. \tag{41}$$

The minimum of $4[\sin^2(\omega t/2)]/\omega^2$ is given by

$$\frac{\omega t}{2} = n\pi \Longrightarrow \omega = \frac{2\pi n}{t}. \tag{42}$$

where $n = \pm 1, \pm 2, \pm 3, \cdots$. Analysing the maximum of this function is given by

$$\begin{aligned} \max_{\omega\approx 0}\left\{\frac{4\left[\sin^2\left(\frac{\omega t}{2}\right)\right]}{\omega^2}\right\} &\cong \max_{\omega\approx 0}\left\{\lim_{\omega\to 0}\frac{4\left[\sin^2\left(\frac{\omega t}{2}\right)\right]}{\omega^2}\right\} = \max_{\omega\approx 0}\left\{\lim_{\omega\to 0}\frac{2\sin\frac{\omega t}{2}\cos\frac{\omega t}{2}}{\omega}t\right\} \\ &= \max_{\omega\approx 0}\left\{\lim_{\omega\to 0}\frac{\sin\omega t}{\omega}t\right\} = \max_{\omega\approx 0}\left\{\lim_{\omega\to 0}\cos(\omega t)\,t^2\right\} = t^2 \end{aligned} \tag{43}$$

We can observe the maximum is proportional to t^2. On the other hand, the amplitude of oscillation is reduced at half of its maximum so we can evaluate the full width at maximum peak height

$$\cos(\omega t)\,t^2 = t^2/2 \to (1-(\omega t)^2/2)t^2 = t^2/2 \to |\Delta\omega| \propto 2/t \tag{44}$$

It is important to notice that as time increases, the first-order term of the expansion is just appreciable for values where oscillations do not cancel. Then

$$\omega t/2 = \pi \to t = 2\pi/|\omega| = 2\pi\hbar/|E_n - E_i| \tag{45}$$

If the time interval of the perturbation is given by Δt and the energy involved in transition is given by $\Delta \mathrm{E} = \mathrm{E}_n - \mathrm{E}_i$, we have the following relation

$$\Delta t \Delta \mathrm{E} \sim \hbar \tag{46}$$[1]

As time interval increases in perturbation, narrower the peak energy and consequently we have a small amount of energy involved, being enough to cause a transition. On the other hand, smaller the time involved, broader is the energy peak and, consequently, the amount of energy involved in the transition is bigger. Thus, for the appreciable transitions, with energy close to the final states, we have

$$\left|c_n^{(1)}\right|^2 = \frac{\left|\mathbf{H}_{ni}^1\right|^2}{\hbar^2}\frac{4[\sin^2(\omega t/2)]}{\omega^2} \cong \frac{\left|\mathbf{H}_{ni}^1\right|^2}{\hbar^2}t^2. \tag{47}$$

The probability of finding the physical system in the state $|n\rangle$ after a time interval of perturbation is linearly proportional to the square of the time. There is, generally, a group of final states $|n\rangle$ in which possess energy very close to the energy of initial state

---

[1] This equation is known as the energy-time uncertainty relation.

$|i\rangle$. Supposing the final states have a continuous spectrum in neighbourhood of the initial state, the total transition of probability is given by

$$\sum_{n,E_n\cong E_i}\left|c_n^{(1)}\right|^2 \Rightarrow \int dN_n\left|c_n^{(1)}\right|^2 = \int d\mathrm{E}_n\rho(\mathrm{E}_n)\left|c_n^{(1)}\right|^2 \tag{48}$$

where in case of a discrete summing has been changed by an integral summed over the density of states with energy interval between E and $\mathrm{E}+d\mathrm{E}$. Replacing the first-order perturbation term into (2.2.13),

$$\int d\mathrm{E}_n\rho(\mathrm{E}_n)\left|c_n^{(1)}\right|^2 = \int d\mathrm{E}_n\rho(\mathrm{E}_n)\frac{4\left|\mathbf{H}_{ni}^1\right|^2}{|\mathrm{E}_n-\mathrm{E}_i|^2}\sin^2[(\mathrm{E}_n-\mathrm{E}_i)t/2\hbar]. \tag{49}$$

For large time intervals[1], the term becomes

$$\lim_{t\to\infty}\frac{1}{|\mathrm{E}_n-\mathrm{E}_i|^2}\sin^2[(\mathrm{E}_n-\mathrm{E}_i)t/2\hbar] = \frac{\pi t}{2\hbar}\delta(E_n-E_i). \tag{50}$$

Replacing this result in Equation (49) and solving the integral, we get

$$\overline{|\mathbf{H}_{n\imath}^1|}^2\frac{2\pi t}{\hbar}\int d\mathrm{E}_n\rho(\mathrm{E}_n)\,\delta(\mathrm{E}_n-\mathrm{E}_i) = \overline{|\mathbf{H}_{n\imath}^1|}^2\left(\frac{2\pi}{\hbar}\right)t\rho(E_n)|_{E_n\cong E_i} \tag{51}$$

We can verify that the probability is proportional to the time interval linearly. In addition, it is convenient to evaluate the transition rate, i.e., the transition probability per unit of time. Then, defining the transition rate as $\mathscr{w}_{i\to[n]}$ as the transition probability per unit of time from initial state to the group of final states with similar energies, it follows

$$\mathscr{w}_{i\to[n]} = \frac{d}{dt}\left(\sum_{n,E_n\cong E_i}\left|c_n^{(1)}\right|^2\right) = \frac{d}{dt}\left(\overline{|\mathbf{H}_{n\imath}^1|}^2\frac{2\pi}{\hbar}t\rho(\mathrm{E}_n)|_{\mathrm{E}_n\cong\mathrm{E}_i}\right). \tag{52}$$

Thus, the transition rate is given by

---

[1] For solving this limit, we have used the delta-function definitions, where $\delta(x)=\lim_{t\to\infty}\frac{\sin xt}{\pi x}$ the fundamental limit is given by $\lim_{t\to\infty}\frac{\sin xt}{xt}=0$. Calling $x=(\mathrm{E}_n-\mathrm{E}_i)/2\hbar$, we have that

$$\frac{t}{4\hbar^2}\lim_{t\to\infty}\frac{1}{\frac{|\mathrm{E}_n-\mathrm{E}_i|^2}{4\hbar^2}t}\sin^2[(\mathrm{E}_n-\mathrm{E}_i)t/2\hbar] = \frac{\pi t}{4\hbar^2}\delta\big((\mathrm{E}_n-\mathrm{E}_i)/2\hbar\big).$$

Using the relation $\delta\big((\mathrm{E}_n-\mathrm{E}_i)/2\hbar\big)=2\hbar\delta(\mathrm{E}_n-\mathrm{E}_i)$, finally we obtain $\frac{\pi t}{4\hbar^2}\delta\big((\mathrm{E}_n-\mathrm{E}_i)/2\hbar\big)=\frac{\pi t}{2\hbar}\delta(\mathrm{E}_n-\mathrm{E}_i)$.

$$w_{i\to[n]} = \overline{|\mathbf{H}^1_{ni}|}^2\frac{2\pi}{\hbar}\rho(\mathrm{E}_n)|_{\mathrm{E}_n\cong\mathrm{E}_i}. \tag{53}$$

On the other hand, the transition rate concerned to the first-order perturbation term is time-independent in this regime. Sometimes, this equation can be written considering a single final state,

$$w_{i\to n} = \mathbf{H}^1_{ni}\frac{2\pi}{\hbar}\delta(\mathrm{E}_n - \mathrm{E}_i). \tag{54}$$

This equation is known as Fermi's Golden Rule. The term $\overline{|\mathbf{H}^1_{ni}|}^2$ that appears in Equation (53) is due to the final states form a quasi-continuum spectrum and they are quite similar. Looking at for the second-order perturbation term Equation (38), and rearranging the terms of the formula, we get

$$c_n^{(2)} = \left(\frac{-i}{\hbar}\right)\sum_m \frac{\mathbf{H}^1_{nm}\mathbf{H}^1_{mi}}{(\mathrm{E}_m - \mathrm{E}_i)}\int_0^t \left(e^{i\omega_{nm}t'} - e^{i\omega_{ni}t'}\right)dt' \tag{55}$$

where $\omega_{nm} + \omega_{mi} = \frac{1}{\hbar}(E_n - E_i) = \omega_{ni}$. The second term in the above integral will lead to the same time-dependence of the first-order perturbation term. By deduction, using the equivalent argument adopted before, the only contribution comes from those energies of final states similar to energy of initial state. Moreover, when the energy of the states $|m\rangle$ differ from $|n\rangle$ and $|i\rangle$, this term contributes for the transition of probability and increases linearly with time as well. Thereby,

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\overline{\left|\mathbf{H}^1_{ni} + \sum_m \frac{\mathbf{H}^1_{nm}\mathbf{H}^1_{mi}}{(E_m - E_i)}\right|}^2 \rho(\mathrm{E}_n)|_{\mathrm{E}_n\cong\mathrm{E}_i}. \tag{56}$$

The transition occurred due the second-order can be described as a transition of two steps. The first one the system undergoes a transition from the initial state $|i\rangle$ to $|m\rangle$ and subsequently to another state $|n\rangle$. These intermediary states are called of virtual states and they require no conservation of energy in the virtual transitions.

4.2 Harmonic Perturbation

Consider now another kind of perturbation, with the term given by

$$\mathbf{H}^1(t) = \mathbf{H}^1 e^{i\omega t} + {\mathbf{H}^1}^{\dagger} e^{-i\omega t} \tag{57}$$

where the operator $\mathbf{H}^1$depends on the space and momentum as well. Taking the same initial conditions treated in the previous section of constant perturbation and replacing the perturbation term in Equation (50), we have

$$c_n^{(1)} = \left(\frac{-i}{\hbar}\right)\left[\mathbf{H}_{ni}^{1}\int_{t_0}^{t} e^{i(\omega+\omega_{ni})t'}dt' + \mathbf{H}_{ni}^{1\dagger}\int_{t_0}^{t} e^{i(-\omega+\omega_{ni})t'}dt'\right] \tag{58}$$

We can compare it with the constant perturbation and we are able to notice that for appreciable transitions in harmonic perturbation, the condition is given by

$$\omega_{ni} \pm \omega \cong 0 \Rightarrow \frac{(\mathrm{E}_n - \mathrm{E}_i)}{\hbar} \pm \omega \cong 0 \Rightarrow \mathrm{E}_n \cong \mathrm{E}_i \mp \hbar\omega. \tag{59}$$

There is no conservation of energy in the harmonic perturbation satisfied by the quantum system alone. The compensation comes from the perturbation part, where in case of absorption process the system receives $\hbar\omega$ of energy from the perturbation term and in the case of emission, the quantum system gives up the excess of $\hbar\omega$ to the perturbation term. Thus, the transition rates for stimulated emission and absorption processes are given by[1]

$$\mathcal{w}_{i\to[n]} = \frac{2\pi}{\hbar}\overline{|\mathbf{H}_{n\iota}^{1}|}^2\rho(\mathrm{E}_n)|_{\mathrm{E}_n\cong\mathrm{E}_i-\hbar\omega} \tag{60}$$

$$\mathcal{w}_{i\to[n]} = \frac{2\pi}{\hbar}\overline{\left|\mathbf{H}_{n\iota}^{1\dagger}\right|}^2\rho(\mathrm{E}_n)|_{\mathrm{E}_n\cong\mathrm{E}_i+\hbar\omega} \tag{61}$$

For summarizing, the constant perturbation has demonstrated that just in case where the energy of the group of final states are near of the energy of the initial states that we obtain appreciable transitions of probability. On the other hand, if the perturbation is harmonic, the real contribution come from transition between the system and the perturbation term as a complete physical system.

5 ABSORPTION AND STIMULATED EMISSION

The interaction of atoms with classical fields is of fundamental importance and requires many complex problems in nature. However, we will consider here in this work just two applications of quantum perturbation theory. The first is the absorption and stimulated emission in hydrogen atom (in which the classical radiation hits the atom and causes a transition between energy levels).

---

[1] We can observe clearly that $\mathbf{H}_{ni}^{1}|n\rangle \Leftrightarrow \langle n|\mathbf{H}_{ni}^{1\dagger}$, i.e., the $\mathbf{H}_{ni}^{1} = \mathbf{H}_{ni}^{1\dagger}$. Thus, $\overline{|\mathbf{H}_{n\iota}^{1}|}^2 = \overline{\left|\mathbf{H}_{n\iota}^{1\dagger}\right|}^2$ and it is evident the symmetry between two processes. The transition rates per unit of density of states are given by

$$\left.\frac{\mathcal{w}_{i\to[n]}}{\rho(\mathrm{E}_n)}\right|_{\mathrm{E}_n\cong\mathrm{E}_i-\hbar\omega} = \frac{2\pi}{\hbar}\overline{|\mathbf{H}_{n\iota}^{1}|}^2 = \frac{2\pi}{\hbar}\overline{\left|\mathbf{H}_{n\iota}^{1\dagger}\right|}^2, = \left.\frac{\mathcal{w}_{n\to[i]}}{\rho(E_n)}\right|_{\mathrm{E}_i\cong\mathrm{E}_n+\hbar\omega}$$

We are in position now to apply quantum perturbation theory in interactions of atom with classical radiation field. Consider the Hamiltonian is given by

$$\mathbf{H} = \frac{\mathbf{p}^2}{2m_e} + e\phi(\mathbf{r}) - \frac{e}{m_e c}\mathbf{A}\cdot\mathbf{p} \tag{62}$$

where $\mathbf{p}^2/2m_e + e\phi(\mathbf{r})$ is the piece of the Hamiltonian that is concerned to the atomic system and the term $(e/m_e c)\mathbf{A}\cdot\mathbf{p}$ of that is related with the interaction between the electromagnetic field with the momentum of the electron. The Equation (62) is valid since the condition $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$.[1] We can define a vector potential of a monochromatic electric field as

$$\mathbf{A} = 2\mathbf{A}_0\cos(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{63}$$

where $\mathbf{A}_0$ and $\mathbf{k}$ are the polarization and the wave vector of the electric field. Writing the vector potential in Euler notation and replacing in the Hamiltonian of the physical system, it results

$$\mathbf{H} = \frac{\mathbf{p}^2}{2m_e} + e\phi(\boldsymbol{x}) - \frac{e}{m_e c}\mathbf{A}_0\cdot\mathbf{p}\left[e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\omega t} + e^{-i\mathbf{k}\cdot\mathbf{r}}e^{i\omega t}\right]. \tag{64}$$

Using the results of the harmonic perturbation obtained in section 2.3, we can define the last term as a perturbation, where the responsible term for the absorption is given by

$$\mathbf{H}_{ni}^{1\dagger} = -\frac{e}{m_e c}\mathbf{A}_0\cdot\mathbf{p}e^{i\mathbf{k}\cdot\mathbf{r}}\Big|_{ni}. \tag{65}$$

Thus, the transition rate of the absorbed energy from an electromagnetic field is then

$$\mathcal{w}_{i\to n} = \frac{2\pi}{\hbar}\frac{e^2}{m_e^2c^2}\left|\langle n|\mathbf{A}_0\cdot\mathbf{p}e^{i\mathbf{k}\cdot\mathbf{r}}\,|i\rangle\right|^2\delta(\mathrm{E}_n - \mathrm{E}_i - \hbar\omega) \tag{66}$$

The final states $|n\rangle$ form a discrete spectrum and due to the fact that they are not in ground state and the function cannot be infinitely sharp, we can verify that the delta-function has a natural broadening due to finite lifetime (BUTKOV, 1973).[2] Henceforth, it is possible obtain the energy cross section of the energy absorbed of the transition as

$$\sigma_{\text{abs}} = \frac{\text{Energy absorbed by the atom (i→n) per unit time}}{\text{Energy flux of ratiation}} \tag{67}$$

---

[1] This condition is called Coulomb gauge.

[2] In general, we regard $\delta(\omega)$ as a Lorentzian function $\delta(\omega) = \lim_{\epsilon\to 0}\frac{1}{\pi}\frac{\epsilon}{\omega^2+\epsilon^2}$. In this sense, applying to the case $\delta(\omega - \omega_{ni}) = \lim_{\zeta\to 0}\frac{1}{2\pi}\frac{\zeta}{(\omega-\omega_{ni})^2+\frac{\zeta^2}{4}}$

Dealing with classical fields, we can use the Maxwell's field equations and obtain the radiation energy from these followings relations

$$\mathbf{E} = -\frac{1}{c}\frac{d\mathbf{A}}{dt} = 2\mathrm{k}\mathbf{A_0}\sin(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{68}$$

$$\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A} = 2\mathrm{kA}_0\boldsymbol{e_z}\sin(\mathbf{k}\cdot\mathbf{r} - \omega t). \tag{69}$$

Thus $\mathbf{B}$ and $\mathbf{E}$ are mutually perpendicular and perpendicular to the wave vector $\boldsymbol{k}$ and they have the same amplitude as we can verify in Equations (68-69). The energy per unit volume is given by (Shankar, 1994)

$$u = \frac{1}{2}\left(\frac{\mathbf{E}^2}{8\pi} + \frac{\mathbf{B}^2}{8\pi}\right) = \frac{k^2|\mathbf{A_0}|^2}{2\pi}. \tag{70}$$

Now, multiplying the energy per unit volume by speed of wave propagation, we obtain the energy flux radiation. Thus,

$$\sigma_{abs} = \frac{\hbar\omega\frac{2\pi}{\hbar}\frac{e^2}{m_e^2c^2}\left|\langle n|\mathbf{A_0}\cdot\mathbf{p}e^{i\mathbf{k}\cdot\mathbf{r}}\,|i\rangle\right|^2\delta(\mathrm{E}_n - \mathrm{E}_i - \hbar\omega)}{\frac{\omega^2|\mathbf{A_0}|^2}{2\pi c}} \tag{71}$$

Rearranging the terms,

$$\sigma_{abs} = \frac{4\pi^2}{\hbar\omega}\frac{e^2}{m_e^2c}\left|\langle n|\boldsymbol{\varepsilon}\cdot\mathbf{p}e^{i\mathbf{k}\cdot\mathbf{r}}\,|i\rangle\right|^2\,\delta(\omega_{ni} - \omega). \tag{72}$$

Using the *electric dipole approximation* to solve the above equation, we must verify the conditions in a proper way. Considering the wavelength of the radiation field larger than the atomic dimension[1], we can expand the exponential and take the relevant term. Then

$$\sigma_{abs} \cong \frac{4\pi^2}{\hbar\omega}\frac{e^2}{m_e^2c}|\langle n|\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|i\rangle|^2\,\delta(\omega_{ni} - \omega). \tag{73}$$

Taking the polarization direction along *x*-axis the wave vector in the *n*-direction, all is necessary to calculate is the matrix element of the momentum operator $\langle n|p_\mathrm{x}|i\rangle$. Using the Ehrenfest theorem (SAKURAI, 1994), we obtain the momentum as a function of the commutator between space and the Hamiltonian

$$[\mathbf{r},\mathbf{H}] = i\hbar\frac{d\mathbf{H}}{d\mathrm{p}} = \frac{i\hbar\mathbf{p}}{m} \Longrightarrow \mathbf{p_x} = -\frac{i}{\hbar}m[\boldsymbol{x},\mathbf{H}]. \tag{74}$$

Calculating the matrix element of the momentum,

---

[1] Taking the energy of the radiation quite similar to the characteristic energy level of the atom,

$$\hbar\omega\sim\frac{Ze^2}{a_0/Z} \cong \frac{Ze^2}{R_{at}}$$

Or, $\frac{2\pi R_{at}}{\lambda} \sim \frac{Z}{137}$. For small values of Z, the approximation can be done for this case, i.e., $e^{i\frac{\omega}{c}\hat{\boldsymbol{n}}\cdot\boldsymbol{x}} \cong 1$.

$$\begin{aligned}\langle n|\mathbf{p}_\mathrm{x}|i\rangle &= -\frac{i}{\hbar}m\langle n|[\boldsymbol{x},\mathbf{H}]|i\rangle = -\frac{i}{\hbar}m\langle n|\mathbf{r}_\mathrm{x}\mathbf{H}-\mathbf{H}\mathbf{r}_\mathrm{x}|i\rangle = -\frac{i}{\hbar}m[\langle n|\boldsymbol{x}\mathbf{H}|i\rangle-\langle n|\mathbf{H}\boldsymbol{x}|i\rangle] \\ &= -\frac{i}{\hbar}m[\langle n|\mathbf{r}_\mathrm{x}|i\rangle \mathrm{E}_i-\langle n|\mathbf{r}_\mathrm{x}|i\rangle \mathrm{E}_n] = im\frac{(\mathrm{E}_n-\mathrm{E}_i)}{\hbar}\langle n|\boldsymbol{x}|i\rangle.\end{aligned} \tag{75}$$

After arranged the terms

$$\langle n|\mathbf{p}_\mathrm{x}|i\rangle = im\omega_{ni}\langle n|\boldsymbol{x}|i\rangle. \tag{76}$$

For the purpose to eliminate the matrix element of $\mathbf{p}_\mathrm{x}$, we must evaluate the matrix elements of the commutator between $\mathbf{p}_\mathrm{x}$ and $\mathbf{x}$. Opening the commutation relation and inserting the unit operator in the coordinate basis,

$$\begin{aligned}\langle n|[\mathbf{p}_\mathrm{x},\boldsymbol{x}]|i\rangle &= \langle n|\mathbf{p}_\mathrm{x}\boldsymbol{x}|i\rangle-\langle n|\boldsymbol{x}\mathbf{p}_\mathrm{x}|i\rangle = \langle n|\mathbf{p}_\mathrm{x}\left(\sum_j|l\rangle\langle l|\right)\boldsymbol{x}|i\rangle-\langle n|\boldsymbol{x}\left(\sum_j|l\rangle\langle l|\right)\mathbf{p}_\mathrm{x}|i\rangle \\ &= \sum_l\langle n|\mathbf{p}_\mathrm{x}|l\rangle\langle l|\boldsymbol{x}|i\rangle-\sum_l\langle n|\boldsymbol{x}|l\rangle\langle l|\mathbf{p}_\mathrm{x}|i\rangle\end{aligned} \tag{77}$$

Using the result of Equation (76) and replace it in Equation (77), we have

$$\langle n|[\mathbf{p}_\mathrm{x},\boldsymbol{x}]|i\rangle = im\left(\sum_l\omega_{nj}\langle n|\boldsymbol{x}|l\rangle\langle l|\boldsymbol{x}|i\rangle-\sum_l\omega_{ki}\langle n|\boldsymbol{x}|l\rangle\langle l|\boldsymbol{x}|i\rangle\right) \tag{78}$$

Doing $n = i$, finally we get

$$\langle i|[\mathbf{p}_\mathrm{x},\boldsymbol{x}]|i\rangle = 2mi\sum_l\omega_{il}|\langle l|\mathbf{x}|i\rangle|^2. \tag{79}$$

Employing the canonical relations (COHEN-TANNOUGJI, et al., 1977),$[\mathbf{p}_\mathrm{i},\mathbf{r}_\mathrm{j}] = -i\hbar\delta_{ij}$ and noticing that l is a mute variable,

$$i\hbar = i\hbar\left(\frac{2m}{\hbar}\sum_n\omega_{ni}|\langle n|\boldsymbol{x}|i\rangle|^2\right). \tag{80}$$

That implicates the term in parenthesis must be equal to unit, i.e.,

$$\sum_n f_{ni} = \frac{2m}{\hbar}\sum_n\omega_{ni}|\langle n|\boldsymbol{x}|i\rangle|^2 = 1 \tag{81}$$

where is defined here as oscillator strength for quantum transitions between the states from $|i\rangle$ to $|n\rangle$. Substituting the result of Equation (76) into Equation (73), we have

$$\sigma_{abs}(\omega) \cong 4\pi^2\alpha\omega_{ni}|\langle n|\boldsymbol{x}|i\rangle|^2\,\delta(\omega_{ni}-\omega). \tag{82}$$

The cross section of the absorbed energy represented here is a function of the angular frequency and exhibits a sharp delta-function-like peak whenever the energy absorbed is close to the energy level spacing. Summing over the angular frequencies and identifying the strength oscillator,

$$\int \sigma_{abs}(\omega)d\omega \cong \frac{2\pi^2\alpha\hbar}{m}\left(\sum_n \frac{2m}{\hbar}\omega_{ni}|\langle n|\boldsymbol{x}|i\rangle|^2\right) = \frac{2\pi^2\alpha\hbar}{m_e} = 2\pi^2 c\left(\frac{e^2}{m_e c^2}\right) \tag{83}$$

By quantum perturbation theory, it has been possible to estimate the cross section of the absorbed energy from a classical radiation using the first-order perturbation and demonstrate that this is a classical result and it is also remarkable, once it was not necessary to explicit the Hamiltonian of the physical system.

CONCLUSION

In this work, we have introduced the basic concepts of quantum perturbation theory and its application in the absorption and stimulated emission. Using concepts of quantum mechanics and evaluating the transition of probabilities of physical systems, we could obtain very important results such as the rate of transition probabilities when a hydrogen atom is excited by a classical radiation.

REFERENCES

BUTKOV, E. *Mathematical Physics.* New York : Adison-Wesley Publishing Company, 1973.

COHEN-TANNOUGJI, C., DIU, B. AND LALOE, F. *Quantum Mechanic.* s.l. : John Wiley & Sons, 1977. p. 914. Vol. 1.

SAKURAI, J.J. *Modern Quantum Mechanics.* Rev. ed. s.l. : Addison-Wesley Publishing Company, Inc., 1994.

SHANKAR, R. *Principles of Quantum Mechanics.* 2 Ed. New York : Plenum Press, 1994. p. 698.

PULICI, A. R., *Tempo de Tunelamento Quântico***,** Votuporanga**:** MOSAICO, v.1, p.43 - 49, 2006**.**