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# Emission spectrum of two-level single molecule *via* photon counting statistics

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**Abstract.** In this paper, we introduce a new way to obtain the emission spectrum of single molecule driven by external field. A virtual probe field is introduced to simulate the vacuum field, which causes the spontaneous emission phenomena of the excited single molecule. The statistical properties of the emission photons caused by the virtual probe field could be used to obtain the emission spectrum of the single molecule system. The results demonstrate the well-known Mollow triplet splitting phenomenon as the single molecule is driven by strong external field.The abstract should provide a brief summary of the main findings of the paper.

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**Key words**: Two-Level System, Emission Spectrum, Generating Function.

## 1 Introduction

The spectrum of the single molecule could be used to directly observe the change of the state of the system. The well-known one is the Autler-Townes splitting [1], which was first observed by Autler and Townes. Generally, a single quantum system (including single atoms, single molecules, and single quantum dots, *etc.*) driven by strong external field, the coupling states to the external field of the single quantum system could be splitting into two sub-states, this is the well known Autler-Townes splitting phenomenon. It has been studied by several groups [2–5]. This splitting reflects in the emission spectrum is also a well known phenomenon — Mollow triplet splitting [6], which was predicted theoretically by Mollow, then several groups have observed the Mollow triplet splitting phenomenon in experiment [7, 8].

Generally, the emission spectrum is considered as a Fourier transformation of the time dependent dipole-dipole correlation [6, 9], which reflect the emission intensity distribution of the emission photon frequency. On the other way, one could directly obtain

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the emission intensity distribution of the emission photon frequency *via* counting the emission photons at frequency $\omega$ [10]. As we all know, the spontaneous emission of an excited quantum system is caused by the vacuum field [11,12], and the vacuum field include all frequency modes [12]. That means we can not get a the frequency distribution of the emission photons directly from the vacuum field. If we introduce a virtual, changeable frequency probe field to simulate a frequency mode of the vacuum field, then one can get the emission photon number at a fixed frequency. By scanning all the frequency modes, one could obtain the emission intensity distribution versus the emission photon frequency $\omega$, and directly obtain the emission spectrum.

In this paper, we demonstrate how to obtain the emission spectrum of a two-level single molecule driven by external field, the generating function approach is employed to obtain the emission intensity (or average emission photons, which is proportional to the emission intensity at fix time $t$) at frequency $\omega$. The generating function approach is well used to discuss the emission photon counting statistical properties [13–22]. It is also used to discuss the emission spectrum of driven single molecule [10]. In Ref. [10] they directly analyze the emission photons, have gotten the emission spectrum and the corresponding Mandel's $Q$ parameter.In this paper, we introduce a new way to obtain the emission spectrum *via* introducing a virtual probe field. The Mandel's $Q$ parameter in this paper is corresponding to the emission photon caused by the probe field, it is different compared with that in the Ref. [10].

This paper organized as follows: In Sec. 2 we briefly review the generating function approach of single molecule for photon counting statistics, and apply the generating function approach to obtain the emission photon number $\langle N\rangle$ and the corresponding Mandel's $Q$ parameter. The numerical results and discussions are demonstrated in Sec. 3. Our conclusions will be presented in Sec. 4.

## 2 Theory

The Hamiltonian of a two-level single molecule system driven by external field (including a pump field and a virtual probe field), can be written as

$$\mathcal{H}=\mathcal{H}_s+\mathcal{V}_{se}+\mathcal{V}_{sp}, \tag{1}$$

where $\mathcal{H}_s$ is the Hamiltonian of the "bare" two-level system, and the $\mathcal{V}_{se}$ is the interaction between the two level system and the pump field, $\mathcal{V}_{sp}$ is the interaction between the two level system and the probe field. The Hamiltonians can be expressed as

$$\begin{aligned}
&\mathcal{H}_s=\hbar\omega_a|a\rangle\langle a|+\hbar\omega_b|b\rangle\langle b|,\\
&\mathcal{V}_{se}=\hbar\Omega\cos(\omega_L t)(|a\rangle\langle b|+|b\rangle\langle a|),\\
&\mathcal{V}_{sp}=\hbar\Omega_p\cos(\omega_p t)(|a\rangle\langle b|+|b\rangle\langle a|),
\end{aligned} \tag{2}$$

where $\Omega\equiv-\boldsymbol{\mu}_{ab}\cdot\mathcal{E}_0/\hbar$, and $\Omega_p\equiv-\boldsymbol{\mu}_{ab}\cdot\mathcal{E}_p/\hbar$ are the Rabi frequencies of the pump field and probe field, respectively, the $\boldsymbol{\mu}_{ab}$ is the transition dipole moment of the ground state

and excited state of the two level system, $\mathcal{E}_0$ and $\mathcal{E}_p$ are the amplitude of the pump field and the probe field, respectively. The density matrix is used to describe the state of the system, and it satisfies the quantum Liouville equation

$$\frac{\partial}{\partial t}\rho(t)=-\frac{i}{\hbar}[\mathcal{H},\rho(t)]+\mathcal{L}\rho(t), \tag{3}$$

the $\mathcal{L}\rho(t)$ describes the spontaneous emission process. As we just concern the probe signals, we introduce an unitary evolution operator as

$$U(t)=\mathcal{T}\exp\left\{\int_0^t d\tau(\mathcal{H}_s+\mathcal{V}_{se})\right\}. \tag{4}$$

Transferring the density matrix $\rho(t)$ into the interaction picture, the density matrix in the interaction picture can be expressed as

$$\sigma(t)=U(t)\rho(t)U^{\dagger}(t). \tag{5}$$

The density matrix $\sigma(t)$ satisfies

$$\frac{\partial}{\partial t}\sigma(t)=-\frac{i}{\hbar}[\mathcal{V}_{sp}^{I}(t),\sigma(t)]+\mathcal{L}^{I}\sigma(t), \tag{6}$$

where $\mathcal{V}_{sp}^{I}(t)=U(t)V_{sp}U^{\dagger}(t)$ is the interaction between the system and the probe field, $\mathcal{L}^{I}=U(t)\mathcal{L}U^{\dagger}(t)$ is the damping operator, and the $\mathcal{L}^{I}$ can be separated into three parts, one is $\mathcal{L}$ which is the main part, and the other parts can be omitted. Here, we assume $\mathcal{L}^{I}\approx\mathcal{L}$. In the interaction picture, the evolution of the density matrix $\sigma(t)$ is determined by the interaction between the system and the probe field, which imply one could directly obtain the emission photon statistical properties caused by the probe field in the interaction picture.

The elements of the density matrix satisfy

$$\begin{aligned}
\dot{\sigma}_{aa}(t)&=-i\Omega_p\cos(\omega_p t)\frac{\Omega^2}{2(\Delta^2+\Omega^2)}K(e^{i\omega_L t}\sigma_{ba}(t)-e^{-i\omega_L t}\sigma_{ab}(t))+\Gamma\sigma_{bb}(t),\\
\dot{\sigma}_{ab}(t)&=-i\Omega_p\cos(\omega_p t)\left(\frac{\Omega\Delta}{\Delta^2+\Omega^2}\sigma_{ab}(t)+\frac{\Omega^2}{2(\Delta^2+\Omega^2)}Ke^{i\omega_L t}(\sigma_{bb}(t)-\sigma_{aa}(t))\right)-\frac{\Gamma}{2}\sigma_{ab}(t),\\
\dot{\sigma}_{ba}(t)&=-i\Omega_p\cos(\omega_p t)\left(\frac{-\Omega\Delta}{\Delta^2+\Omega^2}\sigma_{ba}(t)-\frac{\Omega^2}{2(\Delta^2+\Omega^2)}Ke^{-i\omega_L t}(\sigma_{bb}(t)-\sigma_{aa}(t))\right)-\frac{\Gamma}{2}\sigma_{ba}(t),\\
\dot{\sigma}_{bb}(t)&=-i\Omega_p\cos(\omega_p t)\frac{\Omega^2}{2(\Delta^2+\Omega^2)}K(e^{-i\omega_L t}\sigma_{ab}(t)-e^{i\omega_L t}\sigma_{ba}(t))-\Gamma\sigma_{bb}(t).
\end{aligned} \tag{7}$$

where $K=2-e^{-i\sqrt{\Delta^2+\Omega^2}t}-e^{+i\sqrt{\Delta^2+\Omega^2}t}$, and $\Delta=\omega_L-\omega_{ba}$, and $\Delta_1=\omega_p-\omega_{ba}$ are the detuning frequencies of the pump and probe fields, respectively.

The generating function reads [14, 17]

$$\mathcal{G}(s,t)=\sum_{n=0}^{\infty}\sigma^{(n)}(t)s^n, \tag{8}$$

where $\sigma^{(n)}(t)$ is the density matrix part when the system has emitted $n$ photons. One can obtain the generating functions satisfy

$$\begin{aligned}
\dot{\mathcal{G}}_{aa}&=-i\Omega_p\cos(\omega_p t)\frac{\Omega^2}{2(\Delta^2+\Omega^2)}K(e^{i\omega_L t}\mathcal{G}_{ba}-e^{-i\omega_L t}\mathcal{G}_{ab})+\Gamma s\mathcal{G}_{bb},\\
\dot{\mathcal{G}}_{ab}&=-i\Omega_p\cos(\omega_p t)\left(\frac{\Omega\Delta}{\Delta^2+\Omega^2}\mathcal{G}_{ab}+\frac{\Omega^2}{2(\Delta^2+\Omega^2)}Ke^{i\omega_L t}(\mathcal{G}_{bb}-\mathcal{G}_{aa})\right)-\frac{\Gamma}{2}\mathcal{G}_{ab},\\
\dot{\mathcal{G}}_{ba}&=-i\Omega_p\cos(\omega_p t)\left(\frac{-\Omega\Delta}{\Delta^2+\Omega^2}\mathcal{G}_{ba}-\frac{\Omega^2}{2(\Delta^2+\Omega^2)}Ke^{-i\omega_L t}(\mathcal{G}_{bb}-\mathcal{G}_{aa})\right)-\frac{\Gamma}{2}\mathcal{G}_{ba},\\
\dot{\mathcal{G}}_{bb}&=-i\Omega_p\cos(\omega_p t)\frac{\Omega^2}{2(\Delta^2+\Omega^2)}K(e^{-i\omega_L t}\mathcal{G}_{ab}-e^{i\omega_L t}\mathcal{G}_{ba})-\Gamma\mathcal{G}_{bb}.
\end{aligned} \tag{9}$$

A working generating function is defined as [14, 17]

$$\mathcal{Y}=\sum_i \mathcal{G}_{ii}, \tag{10}$$

where $\mathcal{G}_{ii}$ is the diagonal elements. The average emission photon number from the two level system can be obtained as

$$\langle N\rangle=2\frac{\partial\mathcal{Y}}{\partial s}\bigg|_{s=1}, \tag{11}$$

and Mandel's $Q$ parameter is

$$Q=\frac{\langle N^2\rangle-\langle N\rangle^2}{\langle N\rangle}-1=\left.\frac{\frac{\partial^2\mathcal{Y}}{\partial s^2}-2\left(\frac{\partial\mathcal{Y}}{\partial s}\right)^2}{\frac{\partial\mathcal{Y}}{\partial s}}\right|_{s=1}, \tag{12}$$

and the spectrum is

$$I(\omega)=\frac{d\langle N\rangle(t)}{dt}\bigg|_{\omega}. \tag{13}$$

## 3 Result and discussion

In this section, we demonstrate the results calculated by the method developed in Sec. 2. Fig. 1 shows the typical resonance fluorescence triplet, the circles are the experimental data coming from Ref. [8], the solid line is the theoretical result. The parameters are $\Gamma/2\pi=11MHz$, and $\Omega/2\pi=57MHz$. The probe field Rabi frequency is $\Omega_p\ll\Gamma$. From

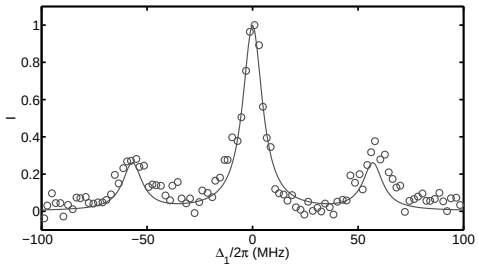


Figure 1: The circles are the experimental data coming from Ref. [8], the spontaneous emission rate $\Gamma/2\pi=11MHz$, the pump Rabi frequency $\Omega/2\pi=57MHz$, the line is calculated by the equation 9.

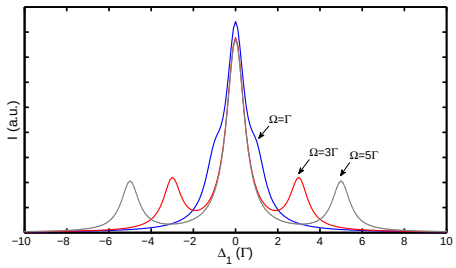


Figure 2: (Color online) The Mollow triple effect are demonstrated, the spontaneous emission rate of the system is $\Gamma=1$, the probe field intensity is $\Omega_p=0.1\Gamma$, the detuning frequency of the pump field is $\Delta=\omega_L-\omega_{ba}=0$.

Fig. 1, one could know that the theoretical result are excellent agreement with the experimental data which coming from Ref. [8].

Fig. 2 shows the resonance fluorescence Mollow triplet at different driven Rabi frequencies. The blue line responds to the driven field $\Omega=\Gamma$, the red line responds to the driven field $\Omega=3\Gamma$, and the black line responds to the driven field $\Omega=5\Gamma$. The figure demonstrates that at $\Omega=\Gamma$ the emission lineshape displays almost one peak, as the driven field increased to $\Omega=3\Gamma$, the lineshape shows explicit three peaks, as the driven field continue increased to $\Omega=5\Gamma$, the three peaks are more separated. This result can be explored by dressed states theory, as the two level system driven by strong pump field, the ground and excited states are split into two sub-ground states and sub-excited states, the electron jump from two sub-excited state to two sub-ground states, which makes three peaks, and the position of the sidebands can be expressed as $r_b=\pm\sqrt{\Delta^2+\Omega^2}$, is decided by the driven Rabi frequency $\Omega$.

According to the dressed states theory, the sidebands position is linear related to the driven Rabi frequency $\Omega$. To make the the linear relationship more clearly, we draw the three dimension figure of the emission intensity as a function of driven Rabi frequency $\Omega$ and probe detuning frequency $\Delta_1$. The results are shown in Fig. 3, upper one is the emission intensity, lower one is the Mandel's $Q$ parameter. From this figure, we can know the splitting of the peaks are linearly increasing as the driven $\Omega$ increasing. As we consider the probe field is very weak $\Omega_p\ll\Gamma$, the Mandel's $Q$ parameter always demonstrates neg-

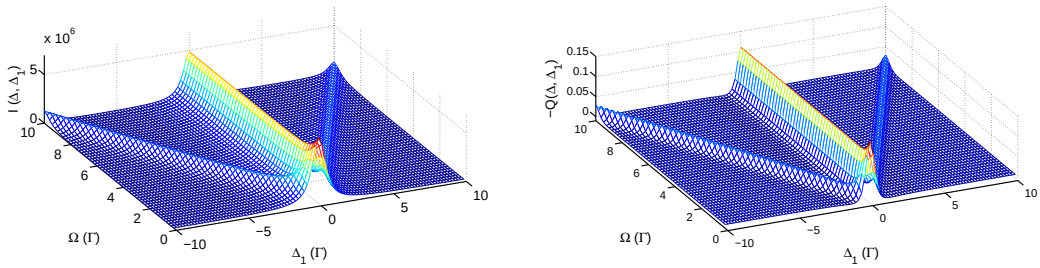


Figure 3: The emission light intensity and Mandel's $Q$ parameter as a function of the probe detuning $\Delta_1$ and pump intensity $\Omega$. The other parameter are $\Gamma/2\pi = 40$MHz, $\Delta = 0$, and $\Omega_p = 0.1\Gamma$.

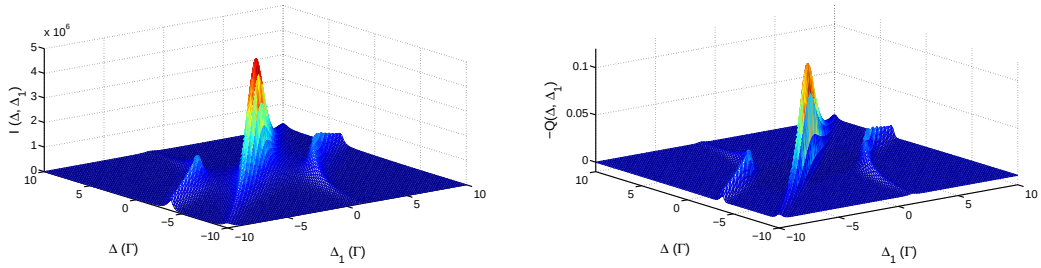


Figure 4: The emission light intensity and Mandel's $Q$ parameter as a function of the detuning frequencies $\Delta$ and $\Delta_1$. The other parameters are $\Gamma/2\pi = 40$MHz, and $\Omega = 5\Gamma$, $\Omega_p = 0.1\Gamma$.

ative, that reflects the emission photon (caused by the probe field) always demonstrate sub Possonian distribution.

We also discussed the driven field is not resonance with the two level system, to make this process more clearly, we draw the emission intensity and its corresponding Mandel's $Q$ parameter as a function of the driven detuning frequency $\Delta$ and probe detuning frequency $\Delta_1$. The results are shown in Fig. 4, when the driven detuning frequency $\Delta = 0$, that means resonance driven, the two small peaks are symmetry distributed beside of the main peak. As the driven detuning frequency $\Delta$ increasing or decreasing, one small peak become closer to the main peak, the other peak become farther to the main peak. The Mandel's $Q$ parameter demonstrates the same behavior as the emission intensity. Because in our condition, the Mandel's $Q$ parameter just reflects the statistical behavior of the emission photon caused by probe field, it is different compared with the result of Ref. [10].

## 4 Conclusion

In this paper, we demonstrate a new way to obtain the emission spectrum of single molecule driven by external field *via* introducing a virtual probe field. The well known

Mollow triplet splitting phenomenon is obtained, and discussed the influence of the Rabi frequency to the emission spectrum and the corresponding Mandel's $Q$ spectrum of the two-level single molecule.

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