# QUANTUM THEORY OF A SPONTANEOUS MANY-PHOTON RAMAN SCATTERING

By D. Welsch

Department of Theoretical Physics, Friedrich Schiller University, Jena*

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By using the momentum-translation approximation the scattering intensity of a many-photon Raman process is quantum theoretically calculated. The result makes it possible to investigate the influence of the light source (for example laser light, thermal light, mixed light) on the scattering intensity found.

## 1. *Introduction*

Reiss [1] has calculated atomic transition probabilities per unit time for a many-photon Raman process in a semiclassical manner and by using the momentum-translation approximation. Such a theory does not explain spontaneous processes, and investigations of the influence of the light source (for example laser light, thermal light, mixed light) on the scattering intensity are very difficult. These difficulties do not occur in a consistent quantum theory that we use here.

Section 2 of this paper is concerned with the application of a general quantum theoretical scattering theory formulated by Knöll [2] to a spontaneous many-photon Raman process.

In Section 3 the high-intensity limit for a laser as a light source, is calculated. The influence of the light source on the scattering intensity is discussed in "first order perturbation theory".

## 2. *The calculation of the scattering intensity*

Knöll [2] has shown that the time derivative of the expectation value of an operator $Q$ within the framework of the scattering theory can be written as

$$\frac{d}{dt}\bar{Q} = \int d\omega \left[\frac{2\pi}{\hbar} \mathrm{Tr}\, \varrho_d(\omega) T^+(\hbar\omega)\delta(\hbar\omega - H_0) Q T(\hbar\omega) + \right.$$

* Address: Friedrich-Schiller-Universität Jena, Fachbereich Theoretische Physik, 69 Jena, Max Wien Platz 1, DDR.

$$+\frac{1}{i\hbar}\,\mathrm{Tr}\,\frac{1}{2}\left[\varrho_d(\omega),\,Q\right](T^+(\hbar\omega)+T(\hbar\omega))-$$

$$\left.-\frac{2\pi}{\hbar}\,\mathrm{Tr}\,\frac{1}{2}\left[\varrho_d(\omega),\,Q\right]_+T^+(\hbar\omega)\delta(\hbar\omega-H_0)T(\hbar\omega)\right] \tag{1}$$

where we have used $[Q,\, H_0] = 0$, and $\varrho_d(\omega) = \delta\left(\omega-\frac{1}{\hbar}H_0\right)\varrho_d$ . $\varrho_d$ is that part of the density operator $\varrho$ (before scattering occurs) the commutator of which with the unperturbed Hamiltonian $H_0$ vanishes. $T(\hbar\omega)$ is given by

$$T(\hbar\omega) = V+VG(\hbar\omega)T(\hbar\omega) \tag{2}$$

with $V$ as the interaction Hamiltonian and with the definition $G(\hbar\omega) = (\hbar\omega-H_0+i\varepsilon)^{-1}$, $\varepsilon\to+0$.

The special case of scattering of electromagnetic radiation by a bound electron (atomic system) leads to

$$H = H_0+V = H_0^E+H_0^F+V,$$

$$V = -\frac{e}{mc}\vec{p}\vec{A}+\frac{e^2}{2mc^2}\vec{A}^2. \tag{3}$$

$H_0^E$ and $H_0^F$ are the unperturbed Hamiltonians of the bound electron and the electromagnetic radiation field (Coulomb gauge); the vector potential $\vec{A}(\vec{x})$ is defined by [2]

$$\vec{A}(\vec{x}) = \sum_{\vec{k}\lambda}\{\vec{A}_{\vec{k}\lambda}(\vec{x})a_{\vec{k}\lambda}+\vec{A}^*_{\vec{k}\lambda}(\vec{x})a^+_{\vec{k}\lambda}\}, \tag{4}$$

$$\vec{A}_{\vec{k}\lambda}(\vec{x}) = \left(\frac{2\pi\hbar c}{L^3k}\right)^{\frac{1}{2}}\vec{e}_{\vec{k}\lambda}e^{i\vec{k}\vec{x}}. \tag{5}$$

From the Appendix 1, the $T$-operator of Eq. (2) which is evaluated by using the machinery of scattering theory is

$$T(\hbar\omega) = Ve^S(1+R(\hbar\omega)W) \tag{6}$$

where we have used the relations

$$R(\hbar\omega) = (\hbar\omega-H'+i\varepsilon)^{-1}, \qquad \varepsilon\to+0, \tag{7}$$

$$H' = e^{-S}He^S = H_0+W, \tag{8}$$

$$S = i\frac{e}{\hbar c}\vec{A}\vec{x} = \sum_{\vec{k}\lambda}S_{\vec{k}\lambda} = i\sum_{\vec{k}\lambda}\hat{S}_{\vec{k}\lambda}\{e^{i\vec{k}\vec{x}}a_{\vec{k}\lambda}+e^{-i\vec{k}\vec{x}}a^+_{\vec{k}\lambda}\}. \tag{9}$$

In the following the dipol approximation will be used. This approximation leads to [3]

$$W \approx -e\vec{x}\vec{E} \tag{10}$$

with $\vec{E}$ as the operator of the electric field strength.

Now, the frequencies of the photons involved in the scattering process are assumed to be very small compared to the energy differences of the bound electron (atomic system). By using the results of Reiss [1] the second term on the right of Eq. (6) can be neglected. We get

$$T(\hbar\omega) \approx Ve^{S}. \tag{11}$$

The use of such a $T$-operator (momentum-translation approximation) is equivalent to the many-photon condition [1].

With the $T$-operator from Eq. (11) we shall treat the spontaneous high-photon Raman transition (see Fig. 1) between the (neighbouring) atomic levels $E_a$, $E_b$ ($H_0^E|a\rangle = E_a|a\rangle$, $H_0^E|b\rangle = E_b|b\rangle$, $E_b - E_a = E_{ba} > 0$). The conservation condition will emerge as

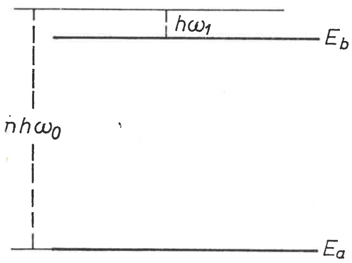


Fig. 1. Schematic of the spontaneous many-photon Raman process

$n\hbar\omega_0 - \hbar\omega_1 - E_{ba} = 0$ ($\omega_0, \omega_1$ — frequencies of the incident and of the scattered wave). To the above effect we identify the operator $Q$ in Eq. (1) with the occupation number operator $N_1 = a_1^+ a_1$ of the scattered light with the assumption $N_1\varrho = \varrho N_1 = 0$ (spontaneous process). The trace (occupation number representation) in Eq. (1) then leads under consideration of the commutator relation

$$a_1 Ve^{S} = [e^{S}(a_1 + i\hat{S}_1 e^{-i\vec{k}\vec{R}}), H_0^E] \tag{12}$$

($\vec{R}$ — position vector of the atom) and by replacing $e^S$ in the sense of a development by $e^{S_0}$ (0 — index of the incident wave) to

$$\frac{d}{dt}\overline{N}_1 = \frac{2\pi}{\hbar}\sum_m \varrho^0_{m+n|m+n} E_{ba}^2\, \delta(n\hbar\omega_0 - \hbar\omega_1 - E_{ba}) \times$$

$$\times \langle a|\hat{S}_1 \langle m+n|e^{-S_0}|m\rangle|b\rangle\, \langle b|\hat{S}_1\langle m|e^{S_0}|m+n\rangle|a\rangle. \tag{13}$$

From the Appendix 2, the matrix element $\langle m|e^{S_0}|n\rangle$ to be calculated is

$$\langle m|e^{S_0}|n\rangle = \sum_{\nu=0}^{l} e^{-\frac{1}{2}\hat{S}_0^2}\, \frac{(m!n!)^{\frac{1}{2}}(i\hat{S}_0 e^{-i\vec{k}\vec{R}})^{m-\nu}(i\hat{S}_0 e^{i\vec{k}\vec{R}})^{n-\nu}}{\nu!(m-\nu)!(n-\nu)!} \tag{14}$$

($l = \min(m, n)$). Thus we get

$$\frac{d}{dt}\overline{N}_1 = \frac{2\pi}{\hbar}\sum_{m=0}^{\infty}\sum_{\nu=0}^{m}\sum_{\mu=0}^{m}\frac{m!(m+n)!}{(m-\nu)!(m-\mu)!}\,\varrho^0_{m+n|m+n}\times$$
$$\times\, T^{\nu}_{nab}T^{\mu}_{nba}\,\delta(n\hbar\omega_0-\hbar\omega_1-E_{ba}) \tag{15}$$

with the abbreviation

$$T^{\nu}_{nab} = \langle a|\hat{S}_1 e^{-\frac{1}{2}\hat{S}_0^2}\frac{(-1)^{\nu}\hat{S}_0^{2\nu+n}}{\nu!(\nu+n)!}|b\rangle\,|E_{ab}|. \tag{16}$$

From the Appendix 3, the $m$-summation in Eq. (15) which is carried out leads to the convenient equation

$$\frac{d}{dt}\overline{N}_1 = \frac{2\pi}{\hbar}\sum_{\nu=0}^{\infty}\sum_{\mu=0}^{\infty}\langle(a_0^+)^n(a_0^+)^{\nu}(a_0)^{\nu}(a_0^+)^{\mu}(a_0)^{\mu}(a_0)^n\rangle\times$$
$$\times\, T^{\nu}_{nab}T^{\mu}_{nba}\,\delta(n\hbar\omega_0-\hbar\omega_1-E_{ba}) \tag{17}$$

where $\langle\ldots\rangle$ means the trace with the density operator $\varrho^0$ (density operator of the incident light).

### 3. Discussion

Eq. (17) is the quantum theoretical generalization of the semiclassical result of Reiss [1]. It clearly shows the influence of the light source on the scattering intensity because the expectation value of the product of the field operators that occurs in Eq. (17) depends on the density operator of the incident wave.

The light source is assumed to be a laser of high intensity. In this case the density operator $\varrho^0$ in the $P$-representation is given by [4]

$$\varrho^0 = \frac{1}{2\pi\sqrt{\overline{N}_0}}\int d^2\alpha\;\delta(|\alpha|-\sqrt{\overline{N}_0})\,|\alpha\rangle\langle\alpha|,\qquad \overline{N}_0 \gg 1 \tag{18}$$

($a_0|\alpha\rangle = \alpha|\alpha\rangle$, $\overline{N}_0 = \langle a_0^+a_0\rangle$ is the mean number of the incident laser photons). By using this density operator the calculation of the expectation value of the products of the field operators in Eq. (17) leads to

$$\langle(a_0^+)^n(a_0^+)^{\nu}(a_0)^{\nu}(a_0^+)^{\mu}(a_0)^{\mu}(a_0)^n\rangle \approx \overline{N}_0^{\,n+\nu+\mu}. \tag{19}$$

Then the $\nu$- and $\mu$-summations in Eq. (17) can be carried out. We get

$$\frac{d}{dt}\overline{N}_1 = \frac{2\pi}{\hbar}E^2_{ba}\,|\langle a|\hat{S}_1 e^{-\frac{1}{2}\hat{S}_0^2}\,J_n(2\hat{S}_0\sqrt{\overline{N}_0})|b\rangle|^2\times$$
$$\times\,\delta(n\hbar\omega_0-\hbar\omega_1-E_{ba}) \tag{20}$$

($J_n(2\vec{S}_0\sqrt{\overline{N}_0})$ — Bessel function). The same result also follows with the density operator $\varrho^0 = |\overline{N}_0\rangle\langle\overline{N}_0|$ $(a_0^+a_0|\overline{N}_0\rangle = \overline{N}_0|\overline{N}_0\rangle)$ with $\overline{N}_0 \gg n$.

In the sense of a generalized perturbation theory we neglect in Eq. (17) terms with $\mu \neq 0$, $\nu \neq 0$. This means

$$\frac{d}{dt}\overline{N}_1 = \frac{2\pi}{\hbar}\langle(a_0^+)^n(a_0)^n\rangle|T^0_{nab}|^2\delta(n\hbar\omega_0-\hbar\omega_1-E_{ba}). \tag{21}$$

If the incident light is laser-like light with the density operator from Eq. (18) then Eq. (21) leads to the result

$$\frac{d}{dt}\overline{N}_1 = \frac{2\pi}{\hbar}(\overline{N}_{0L})^n|T^0_{nab}|^2\delta(n\hbar\omega_0-\hbar\omega_1-E_{ba}) \tag{22}$$

($\overline{N}_{0L}$ — mean number of the incident laser photons). Another case we are interested in is the scattering with thermal light, the density operator of which is [4]

$$\varrho^0 = \frac{1}{\pi\overline{N}_{0T}}\int d^2\alpha\, e^{-\frac{|\alpha|^2}{\overline{N}_{0T}}}|\alpha\rangle\langle\alpha|. \tag{23}$$

From Eq. (21) we get

$$\frac{d}{dt}\overline{N}_1 = \frac{2\pi}{\hbar}n!(\overline{N}_{0T})^n|T^0_{nab}|^2\delta(n\hbar\omega_0-\hbar\omega_1-E_{ba}) \tag{24}$$

($\overline{N}_{0T}$—mean photon number of the incident thermal light). By using a laser and a thermal light source of the same intensity we therefore find for the second case a scattering intensity greater by the factor $n!$. This means that in the case of a thermal light source we need a smaller intensity of the incident wave then that by using a laser if we wish to obtain the same scattering intensity. The density operator $\varrho^0 = |\overline{N}_0\rangle\langle\overline{N}_0|$ leads to the smallest scattering intensity:

$$\frac{d}{dt}\overline{N}_1 = \frac{2\pi}{\hbar}n!\binom{\overline{N}_0}{\overline{N}_0-n}|T^0_{nab}|^2\delta(n\hbar\omega_0-\hbar\omega_1-E_{ba}). \tag{25}$$

It is clear that the number of incident photons $\overline{N}_0$ must be equal at least $n$. In the limit $\overline{N}_0 \gg n$ we get $n!\binom{\overline{N}_0}{\overline{N}_0-n} \approx \overline{N}_0^n$. Eq. (25) and Eq. (22) will be identical.

The influence of quantum statistical properties of light from various sources on non-linear optical processes of low order perturbation theory (one-photon Raman scattering, two-photon absorption *etc.*) was investigated theoretically by Shen [6] (calculation of stationary resolutions of the density matrix equation within the framework of the ordinary time-dependent perturbation theory). For example, the average Stokes generation (one-photon vibrational Raman process) was found to be much more effective by chaotic pumps than by coherent pumps. It can be said that our results for the spontaneous many-photon Raman scattering considered in this paper are a (nonperturbative) generalization (with respect to many-photon processes) of the results derived by Shen [6] on other way.

## APPENDIX 1

The Fourier component of the state vector after the scattering process is shown in [2] to be given by

$$|\Psi(\omega)\rangle = |\Psi^{(0)}(\omega)\rangle + G(\hbar\omega)V|\Psi(\omega)\rangle =$$
$$= |\Psi^{(0)}(\omega)\rangle + G(\hbar\omega)T(\hbar\omega)|\Psi^{(0)}(\omega)\rangle \tag{A.1}$$

where $|\Psi^{(0)}(\omega)\rangle$ is the Fourier component of the state vector before scattering occurs. We consider the unitary transformation described in Eq. (8). The transformed state vector $|\Psi'(\omega)\rangle$ is found to be

$$|\Psi'(\omega)\rangle = e^{-S}|\Psi(\omega)\rangle. \tag{A.2}$$

This transformed state vector can be calculated again within the framework of the scattering theory [2]:

$$|\Psi'(\omega)\rangle = |\Psi^{(0)}(\omega)\rangle + R(\hbar\omega)W|\Psi^{(0)}(\omega)\rangle. \tag{A.3}$$

The definitions of $R(\hbar\omega)$ and $W$ are given in Eq. (7) and in Eq. (8). Combining Eq. (A.3) with Eq. (A.2) and Eq. (A.1) we readily find the $T$-operator given by Eq. (6).

## APPENDIX 2

To prove Eq. (14) we write $e^{S_0}$ as a normal product of the field operators of the incident wave. In the $P$-representation and by developing exponential functions we get

$$\langle m|e^{S_0}|n\rangle = \sum_{\nu=0}^{\infty}\sum_{\mu=0}^{\infty}\sum_{\tau=0}^{\infty} e^{-\frac{1}{2}\hat{S}_0^2}\frac{1}{\pi^2}\int d^2\beta\, d^2\gamma\, e^{-|\beta|^2}e^{-|\gamma|^2}\times$$
$$\times\frac{(i\hat{S}_0e^{-i\vec{k}\vec{R}})^{\mu}(i\hat{S}_0e^{i\vec{k}\vec{R}})^{\tau}\beta^m(\beta^*)^{\mu+\nu}(\gamma^*)^n\gamma^{\nu+\tau}}{(m!n!)^{\frac{1}{2}}\nu!\mu!\tau!}. \tag{A.4}$$

By using the relation [4]

$$\frac{1}{\pi}\int d^2\alpha\,(\alpha^*)^m(\alpha)^n e^{-|\alpha|^2} = n!\delta_{nm} \tag{A.5}$$

we find Eq. (14).

## APPENDIX 3

For the proof of Eq. (17) we write down the matrix element $\varrho^0_{m+n|m+n}$ in the $P$-representation $(a_0|\alpha\rangle = \alpha|\alpha\rangle)$:

$$\varrho^0_{m+n|m+n} = \int d^2\alpha\, P(\alpha)\frac{|\alpha|^{2(m+n)}}{(m+n)!}e^{-|\alpha|^2} \tag{A.6}$$

By rearranging the series of Eq. (15) and under consideration of Eq. (A.6) we get

$$\frac{d}{dt}\bar{N}_1 = \frac{2\pi}{\hbar}\int d^2\alpha \quad P(\alpha)\sum_{\nu=0}^{\infty}\sum_{\mu=0}^{\nu}\sum_{m=\nu}^{\infty}\frac{m!|\alpha|^{2m}}{(m-\nu)!(m-\mu)!}|\alpha|^{2n}e^{-|\alpha|^2}\times$$

$$\times\lambda_{\mu\nu}\{T^{\nu}_{nab}T^{\mu}_{nba}+T^{\mu}_{nab}T^{\nu}_{nba}\}\delta(n\hbar\omega_0-\hbar\omega_1-E_{ba}) \tag{A.7}$$

with the definition

$$\lambda_{\mu\nu} = \begin{cases} 1 & \text{for } \nu \neq \mu \\ \frac{1}{2} & \text{for } \nu = \mu. \end{cases} \tag{A.8}$$

The well known identity

$$\sum_{j=0}^{\mu}\binom{\nu}{j}\binom{m-\nu}{\mu-j} = \binom{m}{\mu} \tag{A.9}$$

leads to the relation

$$\sum_{m=\nu}^{\infty}\frac{m!|\alpha|^{2(m+n)}}{(m-\nu)!(m-\mu)!}e^{-|\alpha|^2} =$$

$$= \sum_{j=0}^{\mu}\frac{\mu!\nu!}{j!(\mu-j)!(\nu-j)!}|\alpha|^{2(n+\mu+\nu-j)}. \tag{A.10}$$

Therefore the $\alpha$-integration in Eq. (A.7) if it is transformed identically gives

$$\int d^2\alpha P(\alpha)\sum_{m=\nu}^{\infty}\frac{m!|\alpha|^{2(m+n)}}{(m-\nu)!(m-\mu)!}e^{-|\alpha|^2} =$$

$$= \sum_{j=0}^{\mu}\frac{\mu!\nu!}{j!(\mu-j)!(\nu-j)!}\langle(a_0^+)^n(a_0^+)^\nu(a_0^+)^{\mu-j}a_0^{\nu-j}a_0^\mu a_0^n\rangle =$$

$$= \sum_{j=0}^{\mu}\frac{\mu!\nu!}{j!(\mu-j)!(\nu-j)!}\langle(a_0^+)^n(a_0^+)^\mu(a_0^+)^{\nu-j}a_0^{\mu-j}a_0^\nu a_0^n\rangle \tag{A.11}$$

where $\langle\ldots\rangle$ is the trace with $\varrho^0$. From the normal-ordering theorem [5]

$$a_0^\nu(a_0^+)^\mu = \sum_{j=0}^{\mu}\frac{\mu!\nu!}{j!(\mu-j)!(\nu-j)!}(a_0^+)^{\mu-j}a_0^{\nu-j},$$

$$a_0^{\mu}(a_0^{+})^{\nu} = \sum_{j=0}^{\mu} \frac{\mu!\nu!}{j!(\mu-j)!(\nu-j)!}(a_0^{+})^{\nu-j}a_0^{\mu-j} \tag{A.12}$$

the combination of Eq. (A.11) with Eq. (A.7) leads to the Eq. (17).

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