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## Multiphoton Absorption and Coherence\*

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We study the probability for multiphoton absorption processes induced by both laser and thermal light acting on an atomic system. When the thermal radiation, suitably filtered, has the same frequency spectrum and the same total energy as the laser packet, we find that the ratio between the relative probabilities for  $s$ -photon absorption can be expressed by

$$(4\pi)^{-1/2(s-1)} s! s^{1/2} (\tau_c/\tau)^{s-1},$$

where  $\tau$  is the time during which the atomic system is illuminated by thermal radiation with coherence time  $\tau_c$ . This shows that multiphoton absorption processes depend on the statistical properties of the incident light, and that the probability induced by the laser packet is certainly greater than that induced by the thermal light if  $s < \tau/\tau_c$ .

### 1. INTRODUCTION

IN the last few years three-photon absorption in both naphthalene<sup>1,2</sup> and anthracene<sup>2</sup> crystals and four-photon absorption in naphthalene crystals<sup>2</sup> have been observed. A fair amount<sup>3-5</sup> of theoretical work has been done with regard to multiphoton processes.<sup>6</sup>

A very interesting problem is to determine if and how much the multiphoton absorption probability depends on the statistical properties of the light used. So the goal of the present work is to evaluate the multiphoton absorption probability both for laser and thermal light within the framework of quantum electrodynamics. This is a natural extension of our previous work on one- and two-photon absorption processes.<sup>7</sup>

In all the experiments carried out up to now, very short wave packets have been used. We find it is important not to suppose that the light is monochromatic, and consequently, we carry on our analysis taking into account the phase of the different Fourier components.

We describe a laser packet of duration  $\tau_l$  and coherence time  $\tau_c$  (defined as  $1/\Delta\nu$ )<sup>8</sup> as a pure coherent polychromatic state with  $\tau_l = \tau_c$ . For the thermal light we use blackbody radiation which is represented by a density operator diagonal in the occupation numbers. This radiation is then supposed to pass through an appropriate linear filter<sup>9</sup> in order to obtain the same spectrum as that of the coherent packet.

In a recent paper, Guccione-Gush, Gush, and Van Kranendonk<sup>10</sup> find for two-photon transitions induced by laser packets the same probability obtained by us in C.F.P., but they find a slightly different probability for two-photon transitions in the case of thermal light. The difference is of a factor  $(2\pi)^{1/2}$  and is due to the different form of the chosen spectra (rectangular for Guccione-Gush *et al.*, and Gaussian in C.F.P.). In the same paper, the authors say that we treat the case of thermal light by putting the atom in a cavity containing blackbody radiation for a length of time  $\tau$  approximately

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<sup>1</sup> S. Singh and L. T. Bradley, *Phys. Rev. Letters* **12**, 612 (1964).

<sup>2</sup> F. Pradère, J. Hanus, and M. Schott, *Compt. Rend.* **262**, 1207 (1966); **263**, 372 (1966).

<sup>3</sup> P. Nelson, *Compt. Rend.* **259**, 2185 (1964); F. Floux, P. Nelson, and P. Veyrie, *ibid.* **261**, 4366 (1965); M. C. Teich and G. J. Wolga, *Phys. Rev. Letters* **16**, 625 (1966); H. F. Hamelka, *Physica* **32**, 779 (1966); S. Singh and J. E. Geusic, *Phys. Rev. Letters* **17**, 865 (1966); H. Barry Bebb, *Phys. Rev.* **153**, 23 (1967); E. M. Logothetis and P. L. Hartman, *Phys. Rev. Letters* **18**, 581 (1967).

<sup>4</sup> R. Wallace, *Mol. Phys.* **11**, 457 (1966); *Phys. Rev. Letters* **17**, 397 (1966).

<sup>5</sup> S. Kielich, *Acta Phys. Polon.* **30**, 393 (1966).

<sup>6</sup> In this paper we limit our study essentially to processes with more than two photons, and so we neglect the bibliography on two-photon transitions.

<sup>7</sup> S. Carusotto, G. Fornaca, and E. Polacco, *Phys. Rev.* **157**, 1207 (1967). In the following we refer to this paper as C.F.P.

<sup>8</sup> L. Mandel and E. Wolf, *Rev. Mod. Phys.* **37**, 231 (1965).

<sup>9</sup> A linear filter is a filter that changes the spectral response but not the statistical properties of radiation.

<sup>10</sup> R. Guccione-Gush, H. P. Gush, and J. Van Kranendonk, *Can. J. Phys.* **45**, 2513 (1967). We compare Eqs. (29) and (38) of this paper with Eqs. (31) and (25) of C.F.P., respectively.

equal to the duration of the laser pulse  $\tau_l$ . Starting from this point they arrive at the conclusion that our comparison between the probabilities induced by thermal radiation and that induced by coherent pulse is questionable. They suggest a comparison of the probability induced by laser pulse with that induced by a thermal pulse (which cannot be represented by a density matrix diagonal in the  $n$  representation, since it is not stationary). We observe that the starting point is due to a misunderstanding; in fact, in C.F.P. and in the present paper, we compare the absorption probability induced by thermal light with that induced by a laser packet when the two radiations have the same spectrum and the same total energy. Therefore, the duration  $\tau$  of thermal light must be much longer than  $\tau_c$  to compensate for the different spectral intensities available.

With the purpose of determining if and how much the multiphoton absorption depends on the statistical properties of the used light, we study the two extreme cases; thermal light and laser pulse. We think that a thermal pulse may be represented, in first approximation, by a density matrix diagonal in the  $n$  representation because  $\tau$  must be much longer than  $\tau_c$ .

With these assumptions we find that the  $s$ -photon transition probability for coherent light is

$$(4\pi)^{-(1/2)(s-1)} s! s^{1/2} (\tau_c/\tau)^{s-1}$$

times the probability for thermal light.

## 2. PROPERTIES OF LASER AND THERMAL RADIATION

For convenience we rewrite in this section some formulas from C.F.P. which will be useful in the sections which follow.

The annihilation operator associated with the vector potential of the field at  $\mathbf{r}$ ,  $t$  in the Heisenberg picture is expressed by

$$\mathbf{A}^{(+)} = \left( \frac{2\pi\hbar c}{L_1 L_2 L_3} \right)^{1/2} \sum_{\mathbf{k}, \mu} k^{-1/2} a_{\mathbf{k}, \mu} \mathbf{e}_{\mathbf{k}, \mu} \exp[i(\mathbf{k} \cdot \mathbf{r} - ckt)], \quad (1)$$

where  $\mathbf{e}_{\mathbf{k}, \mu}$  is a unit vector of polarization  $\mu$  and  $\mathbf{k}$  is the propagation vector.  $L_1$ ,  $L_2$ , and  $L_3$  give the dimensions of the quantization volume in the  $x$ ,  $y$ , and  $z$  directions.

A laser packet is characterized by a density matrix  $\rho_l$  which has the following expression in the Glauber  $P$  representation<sup>11</sup>:

$$\rho_l = \frac{1}{2\pi} \int_0^{2\pi} d\bar{\theta} |\{v_{\mathbf{k}, \mu} \exp(i\bar{\theta})\}\rangle \langle \{v_{\mathbf{k}, \mu} \exp(i\bar{\theta})\}|, \quad (2)$$

where

$$|\{v_{\mathbf{k}, \mu} \exp(i\bar{\theta})\}\rangle = \prod_{\mathbf{k}, \mu} |v_{\mathbf{k}, \mu} \exp(i\bar{\theta})\rangle,$$

and

$$\langle \{v_{\mathbf{k}, \mu} \exp(i\bar{\theta})\}|$$

is a pure coherent state defined by the relation

$$a_{\mathbf{k}, \mu} |v_{\mathbf{k}, \mu} \exp(i\bar{\theta})\rangle = v_{\mathbf{k}, \mu} \exp(i\bar{\theta}) |v_{\mathbf{k}, \mu} \exp(i\bar{\theta})\rangle.$$

For the sake of simplicity we suppose  $v_{\mathbf{k}, \mu}$  to be real, i.e., all the components of the wave packet have the same phase. We recall that  $(v_{\mathbf{k}, \mu})^2$  is the mean number of photons  $\langle n_{\mathbf{k}, \mu} \rangle$  on the  $\mathbf{k}$  mode and polarization  $\mu$ . The  $\bar{\theta}$  integration in (2) is necessary because a high-frequency field never has a definite phase; however, it must be pointed out that such integration does not affect the following results, as may easily be understood. By introducing the Fock states, the expression (2) becomes

$$\rho_l = \sum_{\{n\}, \{m\}} g(\{n\}, \{m\}) |\{n\}\rangle \langle \{m\}|, \quad (3a)$$

where

$$g(\{n\}, \{m\}) = \frac{1}{2\pi} \int_0^{2\pi} d\bar{\theta} \prod_{\mathbf{k}, \mu} \exp[-v_{\mathbf{k}, \mu}^2 + i(n_{\mathbf{k}, \mu} - m_{\mathbf{k}, \mu})\bar{\theta}] \times (v_{\mathbf{k}, \mu})^{n_{\mathbf{k}, \mu} + m_{\mathbf{k}, \mu}} (n_{\mathbf{k}, \mu}! m_{\mathbf{k}, \mu}!)^{-1/2}. \quad (3b)$$

The laser packet is supposed to be nearly monochromatic with central frequency  $ck_0$ , and to consist of plane waves travelling along the  $z$  axis, linearly polarized along the  $x$  axis. With this assumption, and by expressing the mean density of the photons in the different  $ck$  frequencies with

$$N(k) = \pi^{-1/2} n l \exp[-l^2(k - k_0)^2], \quad (4)$$

where  $l$  is much higher than  $1/k_0$  and  $n$  is the mean number of photons in the laser packet, we obtain for the total energy per unit area

$$I_{Tl} = \hbar c k_0 n_0, \quad (5)$$

where  $n_0 = n/L_1 L_2$  is the total number of photons per unit area. The expression (5) has been obtained by going into the continuum in the usual way:

$$\frac{1}{L_3} \sum_{\mathbf{k}} \cdots \rightarrow \frac{1}{2\pi} \int dk, \\ \langle n_{\mathbf{k}} \rangle \cdots \rightarrow (2\pi/L_3) N(k). \quad (6)$$

The thermal-light density operator  $\rho_t$  in the Fock representation is diagonal and has the following form<sup>8</sup>:

$$\rho_t = \sum_{\{n\}} f(\{n\}) |\{n\}\rangle \langle \{n\}|, \quad (7a)$$

where

$$f(\{n\}) = \prod_{\mathbf{k}, \mu} [(1 + \langle n_{\mathbf{k}, \mu} \rangle)(1 + 1/\langle n_{\mathbf{k}, \mu} \rangle)^{n_{\mathbf{k}, \mu}}]^{-1}, \quad (7b)$$

and  $\langle n_{\mathbf{k}, \mu} \rangle$  is the average number of photons in the  $\mathbf{k}, \mu$  mode. If now the thermal radiation, after the linear filter, has the same spectrum as our laser packet, we can use Eq. (4) and obtain for the radiation intensity

<sup>11</sup> R. Glauber, Phys. Rev. **131**, 2766 (1963).

(energy per unit area and time)

$$I_{Tt} = \hbar c^2 k_0 n_1, \quad (8)$$

where

$$n_1 = n/L_1 L_2 L_3$$

represents the average photon density.

### 3. INTERACTION HAMILTONIAN

A system of particles in the presence of a radiation field can be described by a Hamiltonian

$$H = H_p + H_r + H_{\text{int}} = H_0 + H_{\text{int}},$$

where  $H_p$  refers to the particles,  $H_r$  refers to the radiation field, and  $H_{\text{int}}$  represents the interaction between the particles and the field;  $H_0$  is defined as  $H_p + H_r$ .

The nonrelativistic interaction Hamiltonian is

$$H_{\text{int}} = -(e/mc)\mathbf{A} \cdot \mathbf{p} + (e^2/2mc^2)\mathbf{A}^2, \quad (9)$$

where the symbols in this expression have the usual meaning. The  $H_{\text{int}}$  operator can be rewritten in the following form<sup>12</sup>:

$$H_{\text{int}} = -(e/c)\mathbf{r} \cdot (\partial\mathbf{A}/\partial t) + (e/mc)\mathbf{p} \cdot (\nabla\mathbf{A} \cdot \mathbf{r}) + (e^2/2mc^2)(\nabla\mathbf{A} \cdot \mathbf{r})^2, \quad (10)$$

where  $\nabla\mathbf{A}$  is the dyadic  $\partial A_i/\partial x_j$ .

We expand Eq. (10) in power series of  $\mathbf{r}$  about the point  $\mathbf{r} = \mathbf{r}_0$ . The term in the first power of  $\mathbf{r}$  comes only from the first addend of (10) and expresses the electric dipole interaction; only this term was used by Göppert-Mayer<sup>13</sup> in her study of two-photon processes. No linear term in  $\mathbf{r}$  actually comes from the second addend in (10) since

$$(\hat{p}_x)_{nn'} = im\omega_{nn'}x_{nn'}.$$

The bilinear terms, which come from both the first and the second addend, express the magnetic dipole and the electric quadrupole interactions.<sup>14</sup> All other terms express interactions of a higher order. Also, the third addend of (10) gives a bilinear term in  $\mathbf{r}$ , but this term, quadratic in  $\mathbf{A}$ , does not contribute to one-photon transitions. Taking into account the parity selection rule, we find that the lowest-order transitions that this term can give rise to are ( $E1E3+M1M1$ ). We observe in addition that, the power-series expansion of the second term of the Hamiltonian (9) contains the first power of  $\mathbf{r}$  which contributes to ( $E1E2+E1M1$ ) transitions.<sup>15</sup>

The above considerations show that the contribution to the multiphoton transition probability given by  $(e^2/2mc^2)(\nabla\mathbf{A} \cdot \mathbf{r})^2$  is negligible when compared to

that given by  $(e^2/2mc^2)\mathbf{A}^2$ . This same conclusion was reached by Wallace<sup>4</sup> in a more complicated way.

In a work of Cohan and Hameka<sup>16</sup> it is asserted that in evaluating the probability for multiphoton (more than two photons) transitions, all contributions of  $H''$  to the transition probability cancel; in such a statement,  $H''$  is the quadratic term in  $\mathbf{A}$  which appears in (9),  $\mathbf{A}$  being assumed constant in all the atomic volume. This last assumption, however, is justified only for  $E1$  transitions; in fact, for other transitions ( $E2, M1, \dots$ ) we must expand  $\mathbf{A}$  in a power series of  $\mathbf{r}$ .

Let us now consider plane waves incident along the  $z$  axis and linearly polarized along the  $x$  axis. To simplify the formulas even more, we suppose the atomic system to be localized at the origin of the coordinate system. Consequently, the contribution of the linear terms in  $\mathbf{r}$  ( $E1$  transition) in (10) is, recalling (1),

$$\mathfrak{D} = \left( \frac{2\pi\hbar c}{L_1 L_2 L_3} \right)^{1/2} iD \sum_k k^{-1/2} a_k, \quad (11a)$$

in which

$$D = ex, \quad (11b)$$

and the contribution of the bilinear terms in  $\mathbf{r}$  ( $E2+M1$  transitions) is

$$\mathfrak{F} = \left( \frac{2\pi\hbar c}{L_1 L_2 L_3} \right)^{1/2} \sum_k k^{1/2} F(k) a_k, \quad (12a)$$

with

$$F(k) = e[(i/mc)\hat{p}_x x - kxz]. \quad (12b)$$

We introduce now the time evolution operator  $U(t_2; t_1)$  of the system and the  $S$  operator, which in the Dirac picture is related to the  $U(t_2; t_1)$  operator by the formal expression

$$S = U(+\infty; -\infty).$$

By using the definition

$$\mathfrak{C}_{\text{int}} = \exp(iH_0 t/\hbar) H_{\text{int}} \exp(-H_0 t/\hbar),$$

where  $H_{\text{int}}$  is the Schrödinger interaction operator, we can write the  $U$  operator in the following way<sup>17</sup>:

$$U = 1 + U_1 + U_2 + \dots + U_s + \dots,$$

with

$$U_s(t_2; t_1) = \left( -\frac{i}{\hbar} \right)^s \int_{t_1}^{t_2} d\tau_1 \int_{t_1}^{\tau_1} d\tau_2 \int_{t_1}^{\tau_2} d\tau_3 \dots \int_{t_1}^{\tau_{s-1}} d\tau_s \times \mathfrak{C}_{\text{int}}(\tau_1) \mathfrak{C}_{\text{int}}(\tau_2) \dots \mathfrak{C}_{\text{int}}(\tau_s). \quad (13)$$

Thus it is evident that the term  $U_s(t_2; t_1)$  gives a contribution to the  $s$ -photon transitions, if we neglect the term bilinear in  $\mathbf{A}$  of  $H_{\text{int}}$ .

<sup>12</sup> P. I. Richard, Phys. Rev. **73**, 254 (1948); E. A. Power and S. Zienan, Nuovo Cimento **6**, 7 (1957).

<sup>13</sup> M. Göppert-Mayer, Ann. Physik **9**, 273 (1931).

<sup>14</sup> R. Guccione and J. Van Kranendonk, Phys. Rev. Letters **14**, 583 (1965).

<sup>15</sup> We neglect the zero-power term which contributes only to Rayleigh scattering.

<sup>16</sup> N. V. Cohan and H. F. Hameka, Phys. Rev. Letters **16**, 478 (1966).

<sup>17</sup> See, for instance, S. Schweber, *Relativistic Quantum Field Theory* (Harper and Row Publishers, Inc., New York, 1954), Secs. 11.C and 11.E.

Now, in Eq. (13), we should replace the  $\mathcal{H}_{\text{int}}$  operator with the  $\mathcal{D}+\mathcal{F}$  operator, but, for the sake of simplicity, we omit the contribution given by  $\mathcal{F}$ , which has opposite parity. In this way we analyze  $(E1)^s$  transitions. When, however, the  $(E1)^s$  transition is forbidden by parity selection rules, we must study the  $[(E1)^{s-1}(E2+M1)]$  transition, and this can easily be done by replacing any  $\mathcal{D}$  operator with an  $\mathcal{F}$  operator. This procedure is the natural generalization of the work by Guccione and Van Kranendonk<sup>14</sup> on two-photon absorption. For a further generalization of these formulas to multiphoton processes of higher order, it is useful to consult Kielich's paper.<sup>5</sup>

#### 4. MULTIPHOTON ABSORPTION WITH A LASER PACKET

Let  $|i\rangle$  and  $|f\rangle$  be two stationary states of the atomic system having the energies  $E_{pi}$  and  $E_{pf}$ .

Before the interaction the atom and the field are uncoupled and, consequently, one can assume that

$$\rho_{Ti} = \rho_i \rho_{pi},$$

where  $\rho_{pi} = |i\rangle\langle i|$  is the density operator of the atom on the initial state  $|i\rangle$  and  $\rho_i$  is the density operator of the field, which we suppose to be the laser packet described by (3).

In order to study the rate at which  $s$ -photon absorption induced by a laser packet takes place, the total density operator  $\rho_{Tf}$  after interaction can be related to the matrix  $\rho_{Ti}$  by the following expression:

$$\rho_{Tf} = S_s \rho_{Ti} S_s^\dagger, \quad (14)$$

where  $S_s = U_s(+\infty; -\infty)$ . The transition probability of the atom to the state  $|f\rangle$  is given by

$$P_{i \rightarrow f}^{(s)} = \text{Tr}\{\rho_{Tf} |f\rangle\langle f|\}.$$

So, recalling (3a), we have

$$\text{Tr}\{\rho_{Tf} |f\rangle\langle f|\} = \sum_{\{n\}, \{m\}} g(\{n\}, \{m\}) \langle h_{s, \{m\}} | h_{s, \{n\}} \rangle, \quad (15)$$

where  $|h_{s, \{n\}}\rangle$  is defined by the expression

$$\begin{aligned} |h_{s, \{n\}}\rangle &= \langle f | S_s | \{n\}, i \rangle = \left( -\frac{i}{\hbar} \right)^s \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \\ &\times \int_{-\infty}^{t_{s-1}} dt_s \langle f | \exp(iH_0 t_1 / \hbar) \mathcal{D} \exp[iH_0(t_2 - t_1) / \hbar] \\ &\times \mathcal{D} \cdots \mathcal{D} \exp(-iH_0 t_s / \hbar) | \{n\}, i \rangle, \end{aligned}$$

and  $\langle h_{s, \{m\}} |$  is defined in a similar way. A straightforward, but somewhat lengthy calculation, yields

$$\begin{aligned} |h_{s, \{n\}}\rangle &= i^{3s-1} \hbar^{-1} \left( \frac{2\pi\hbar c}{L_1 L_2 L_3} \right)^{s/2} \prod_{l=1}^s \sum_{k_l} (n_{k_l} k_l)^{1/2} \langle f | DR(\sum_{l=2}^s k_l) DR(\sum_{l=3}^s k_l) D \cdots DR(k_s) D | i \rangle \\ &\times \int_{-\infty}^{+\infty} dt \exp\{i[E_{pf} - E_{pi} - \hbar c(\sum_{l=1}^s k_l)]t / \hbar\} | \{n_k - \sum_{l=1}^s \delta_{k, k_l}\} \rangle, \quad (16) \end{aligned}$$

where

$$R(k) = (H_p - E_{pi} - \hbar ck)^{-1}.$$

Therefore, from (15) and (16) we have

$$\begin{aligned} \text{Tr}\{\rho_{Tf} |f\rangle\langle f|\} &= \frac{1}{\hbar^2} \left( \frac{2\pi\hbar c}{L_1 L_2 L_3} \right)^s \sum_{\{n\}, \{m\}} g(\{n\}; \{m\}) \prod_{l=1}^s \prod_{j=s+1}^{2s} \sum_{k_l, k_j} (n_{k_l} m_{k_j} k_l k_j)^{1/2} \langle f | DR(\sum_{l=2}^s k_l) DR(\sum_{l=2}^s k_l) D \cdots \\ &\times DR(k_s) D | i \rangle \langle i | D^\dagger R^\dagger(k_{2s}) D^\dagger \cdots D^\dagger R^\dagger(\sum_{j=s+3}^{2s} k_j) D^\dagger R^\dagger(\sum_{j=s+2}^{2s} k_j) D^\dagger | f \rangle \\ &\times \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \exp\{i[E_{pf} - E_{pi} - \hbar c(\sum_{l=1}^s k_l)]t_1 / \hbar - i[E_{pf} - E_{pi} - \hbar c(\sum_{j=s+1}^{2s} k_j)]t_2 / \hbar\} \\ &\times \langle \{m_k - \sum_{j=s+1}^{2s} \delta_{k, k_j}\} | \{n_k - \sum_{l=1}^s \delta_{k, k_l}\} \rangle. \quad (17) \end{aligned}$$

Recalling (3b) and that  $v_k = \langle n_k \rangle^{1/2}$  we have

$$\sum_{\{n\}, \{m\}} g(\{n\}; \{m\}) \prod_{l=1}^s \prod_{j=s+1}^{2s} (n_{k_l} m_{k_j})^{1/2} \langle \{m_k - \sum_{j=s+1}^{2s} \delta_{k, k_j}\} | \{n_k - \sum_{l=1}^s \delta_{k, k_l}\} \rangle = \prod_{l=1}^{2s} \langle n_{k_l} \rangle^{1/2}.$$

If we take into account this result, and if we go into the continuum by means of Eq. (6), we rewrite Eq. (17) in the following form:

$$\begin{aligned} \text{Tr}\{\rho_{Tf}|f\rangle\langle f|\} &= (2\pi)^2(\hbar c)^{s-2}(L_1L_2)^{-s} \left[ \prod_{l=1}^{2s} \int dk_l k_l^{1/2} N^{1/2}(k_l) \right] \delta[k_{fi} - (\sum_{l=1}^s k_l)] \delta[k_{fi} - (\sum_{l=s+1}^{2s} k_l)] \\ &\times \langle f|DR(\sum_{l=2}^s k_l)DR(\sum_{l=3}^s k_l)D \cdots DR(k_s)D|i\rangle \langle i|D^\dagger R^\dagger(k_{2s})D^\dagger \cdots D^\dagger R^\dagger(\sum_{l=s+3}^{2s} k_l)D^\dagger R^\dagger(\sum_{l=2}^{2s} k_l)D^\dagger|f\rangle, \quad (18) \end{aligned}$$

with

$$ck_{fi} = \omega_{fi} = \hbar^{-1}(E_{pf} - E_{pi}).$$

Now we introduce (4) in (18) and perform the integrations recalling the results presented in the Appendix. So Eq. (18) becomes

$$\begin{aligned} \text{Tr}\{\rho_{Tf}|f\rangle\langle f|\} &= (2/s)(1/\hbar c)^2(\pi l^2)^{-\frac{1}{2}s+1} \\ &\times (2\pi\hbar cn/sL_1L_2)^s k_{fi}^s |\langle f|DR[(s-1)k_{fi}/s] \\ &\times DR[(s-2)k_{fi}/s]D \cdots DR[(1/s)k_{fi}]D|i\rangle|^2 \\ &\times \exp[-(l^2/s)(k_{fi} - sk_0)^2]. \end{aligned}$$

By using Eq. (5) this equation can be rewritten as

$$\begin{aligned} P_{i \rightarrow f}^{(s)} &= (2/s)^{s+1} \pi^{\frac{1}{2}s+1} \hbar^{-2} c^{-s} (\Delta\omega)^{s-2} (k_{fi}/k_0)^s I_{Ti}^s \\ &\times \exp[-(l^2/s)(k_{fi} - sk_0)^2] |\langle f|DR[(s-1)k_{fi}/s] \\ &\times DR[(s-2)k_{fi}/s]D \cdots DR[(1/s)k_{fi}]D|i\rangle|^2, \quad (19) \end{aligned}$$

where  $\Delta\omega = c/l$  is the spectral width of the laser packet.<sup>18</sup>

We point out that the expression (19) is valid when the bandwidth  $\Delta\omega$  of the incident radiation is much larger than the width  $\delta\omega$  of the absorption line. But if the upper level belongs to a band and  $s\Delta\omega \ll \delta\omega$ , we must introduce the energy distribution function  $\rho(\omega - \omega_c)$  which we suppose normalized,

$$\int_0^\infty \rho(\omega - \omega_c) d\omega = 1.$$

In this case we get for the  $s$ -photon absorption probability

$$\begin{aligned} \bar{P}_{i \rightarrow f}^{(s)} &= 2^{s+1} s^{-1/2} \pi^{\frac{1}{2}(s+3)} \hbar^{-2} c^{-s} (\Delta\omega)^{s-1} \rho(s\omega_0 - \omega_c) I_{Ti}^s \\ &\times |\langle f|DR[(s-1)k_0]DR[(s-2)k_0]D \cdots \\ &\times DR(k_0)D|i\rangle|^2. \quad (20) \end{aligned}$$

$$\begin{aligned} \text{Tr}\{\rho_{Tf}|f\rangle\langle f|\} &= \hbar^{-2} \left( \frac{2\pi\hbar c}{L_1L_2L_3} \right)^s \sum_{\{n\}} f(\{n\}) \left[ \prod_{l=1}^{2s} \sum_{k_l} (n_{k_l} k_l)^{1/2} \right] \langle f|DR(\sum_{l=2}^s k_l)DR(\sum_{l=3}^s k_l)D \cdots DR(k_s)D|i\rangle \\ &\times \langle i|D^\dagger R^\dagger(k_{2s})D^\dagger \cdots D^\dagger R^\dagger(\sum_{l=s+3}^{2s} k_l)D^\dagger R^\dagger(\sum_{l=s+2}^{2s} k_l)D^\dagger|f\rangle \langle \{n_k - \sum_{l=s+1}^{2s} \delta_{k,k_l}\} | \{n_k - \sum_{l=1}^s \delta_{k,k_l}\} \rangle \\ &\times \int_0^\tau dt_1 \int_0^\tau dt_2 \exp\{i[E_{pf} - E_{pi} - \hbar c(\sum_{l=1}^s k_l)]t_1/\hbar - i[E_{pf} - E_{pi} - \hbar c(\sum_{l=s+1}^{2s} k_l)]t_2/\hbar\}. \quad (21) \end{aligned}$$

<sup>18</sup> For  $s=1$ , Eq. (19) becomes the well-known formula

$$P_{i \rightarrow f}^{(1)} (2\pi/\hbar c)^2 |\langle f|D|i\rangle|^2 I(k_{fi}),$$

where, according to the Eq. (10) of C.F.P.,

$$I(k) = \pi^{-1/2} l^2 (k/k_0) \exp[-l^2(k - k_0)^2] I_{Ti}.$$

If there is a spectroscopic line between the  $i$  and  $f$  levels, we can assume

$$\rho(\omega) = g(\omega),$$

where  $g(\omega)$  is the line-shape function.

## 5. MULTIPHOTON ABSORPTION WITH THERMAL LIGHT

If we consider the radiation field as consisting of thermal radiation, then the density operator  $\rho_{Ti}$  of the atom and the field before interaction is diagonal, and is given by

$$\rho_{Ti} = \rho_i |i\rangle\langle i| = \sum_{\{n\}} f(\{n\}) |i, \{n\}\rangle \langle i, \{n\}|,$$

where  $f(\{n\})$  is defined in Eq. (7b). We suppose that the atom interacts with the field in the time interval  $(0-\tau)$  which is large compared to characteristic time of atomic transitions and to the coherence time of radiation.

Now the density matrix after interaction is related to  $\rho_{Ti}$  by

$$\rho_{Tf} = U_s \rho_{Ti} U_s^\dagger,$$

where  $U_s$ , expressed by (13), is valued for  $t_1=0$  and  $t_2=\tau$ . According to this assumption, Eq. (17) will still be valid, provided that we replace  $S_s$  by  $U_s(0; \tau)$  and  $\sum_{\{n\}, \{m\}} g(\{n\}, \{m\})$  by  $\sum_{\{n\}, \{m\}} f(\{n\}) \delta_{\{n\}, \{m\}}$ . The latter substitution is necessary because of the different structure of the density operator of the field. Therefore, the  $s$ -photon transition probability is given by the expression

If we recall the equality

$$\sum_{\{n\}} f(\{n\}) \prod_{l=1}^{2s} (n_{kl})^{1/2} \langle \{n_k - \sum_{l=s+1}^{2s} \delta_{k,k_l}\} | \{n_k - \sum_{l=1}^s \delta_{k,k_l}\} \rangle$$

$$= \sum_{i=1}^s \prod_{l=1}^s \delta_{k_i, k_l} \langle n_{k_i} \rangle,$$

then, after going into the continuum, Eq. (21) becomes

$$\text{Tr}\{\rho_{Tf} | f \rangle \langle f | \} = \frac{2\pi\tau}{s\hbar^2} \left( \frac{2\pi\hbar c}{L_1 L_2 L_3} \right)^s \left[ \prod_{l=1}^s \int dk_l N(k_l) k_l \right]$$

$$\times \delta[k_{fi} - (\sum_{l=1}^s k_l)] | \langle f | \sum_{l=1}^s [DR(\sum_{i=1}^s k_i) \cdots$$

$$\times DR(\sum_{i=l-1}^s k_i) DR(\sum_{i=l+1}^s k_i) \cdots D] | i \rangle |^2. \quad (22)$$

In this equation we used the approximation, generally employed in perturbation problems, that

$$\left| \int_0^\tau dt \exp\{i[E_{pf} - E_{pi} - \hbar c(\sum_{l=1}^s k_l)]t/\hbar\} \right|_2$$

$$\approx \frac{2\pi\tau}{c} \delta[k_{fi} - (\sum_{l=1}^s k_l)].$$

We recall that we suppose the spectrum of thermal radiation to be equal to that of the coherent packet. So from (22) and (4), making use of the results in the Appendix, the  $s$ -photon absorption probability induced by thermal light can be expressed in the form

$$\bar{P}_{i \rightarrow f}^{(s)} = (2/s c)^{s+1} s! s^{1/2} \hbar^{-2} \pi^{s+1/2} (l/\tau^{s-1}) (k_{fi}/k_0)^2 I_{\tau t}^s$$

$$\times | \langle f | DR[(s-1)k_{fi}/s] DR[(s-2)k_{fi}/s] D \cdots$$

$$\times DR[(1/s)k_{fi}] D | i \rangle |^2$$

$$\times \exp[-(l^2/s)(k_{fi} - sk_0)^2], \quad (23)$$

where  $I_{\tau t}$  expresses the energy irradiated in time  $\tau$ .  $I_{\tau t}$  can be written, with the help of (8), as  $I_{\tau t} = \tau I_{Tt}$ .

Now it is convenient to introduce the radiation bandwidth  $\Delta\omega$  and its coherence time  $\tau_c$ ; this allows us to write the  $s$ -photon absorption probability, expressed by (23), in the form

$$\bar{P}_{i \rightarrow f}^{(s)} = 4\pi^{3/2} s! s^{-(s+1/2)} \hbar^{-2} c^{-s} (\Delta\omega)^{s-2} (\tau_c/\tau)^{s-1} (k_{fi}/k_0)^s$$

$$\times | \langle f | DR[(s-1)k_{fi}/s] DR[(s-2)k_{fi}/s] D \cdots$$

$$\times DR[(1/s)k_{fi}] D | i \rangle |^2$$

$$\times \exp[-(l^2/s)(k_{fi} - sk_0)^2] I_{\tau t}^s. \quad (24)$$

Equation (24) gives the transition probability when  $\delta\omega \ll \Delta\omega$ , i.e., when the absorption linewidth is much smaller than the width of the incident radiation.

On the other side, if  $s\Delta\omega \ll \delta\omega$  we can easily perform calculations as in the preceding section for the similar conditions.

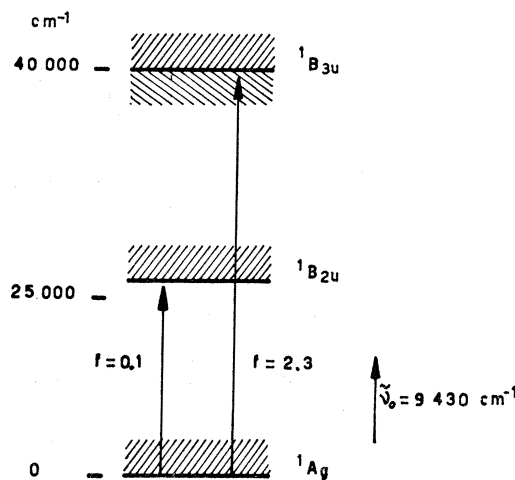


FIG. 1. Energy-band diagram of crystalline anthracene.

## 6. DISCUSSION AND CONCLUSIONS

If we compare Eqs. (21) and (24), which express, respectively, the  $s$ -photon absorption probability for the laser light and for the thermal light, we see that this probability depends on the statistical properties of the light employed; in fact, the ratio  $B_s$  between the  $s$ -photon absorption probability for the thermal light and that for the laser light is given by

$$B_s = \bar{P}_{i \rightarrow f}^{(s)} / P_{i \rightarrow f}^{(s)} = (4\pi)^{-\frac{1}{2}(s-1)} s! s^{1/2} (\tau_c/\tau)^{s-1}. \quad (25)$$

In order to analyze (25) it is useful, now, to introduce the ratio  $B_s/B_{s-1}$ , which is

$$B_s/B_{s-1} \approx 2^{-1/2} s (\tau_c/\tau). \quad (26)$$

From (26) we see that the ratio  $B_s/B_{s-1}$  increases when  $s$  increases, but because normally it is  $s < \tau/\tau_c$ , this ratio remains smaller than one. This shows that normally the highest value for the  $s$ -photon absorption probability is obtained with laser rather than with thermal light.

The presence in (24) of the multiplicative factor  $s!$  is to be attributed to the fact that all Gaussian processes, like the fields produced by thermal sources, are entirely described by their first and second moments. In other words, this factor has the same origin and expresses the same properties as the  $N!$  factor which is present in Eq. (4.36) of Mandel and Wolf's paper.<sup>8</sup>

## 7. DISCUSSION OF EXPERIMENTAL RESULTS

In this last section we attempt to compare the theoretical expressions we have obtained with the experimental results by Pradère *et al.*<sup>2</sup> and by Singh and Bradley.<sup>1</sup> They focused laser beams on crystals and observed three-photon absorption by measuring fluorescent emission. They studied in particular the  ${}^1A_g \rightarrow {}^1B_{2u}$  transition in anthracene (Fig. 1) with neodymium laser light ( $\nu_0 = 9430 \text{ cm}^{-1}$ ) and the  ${}^1A_g \rightarrow$

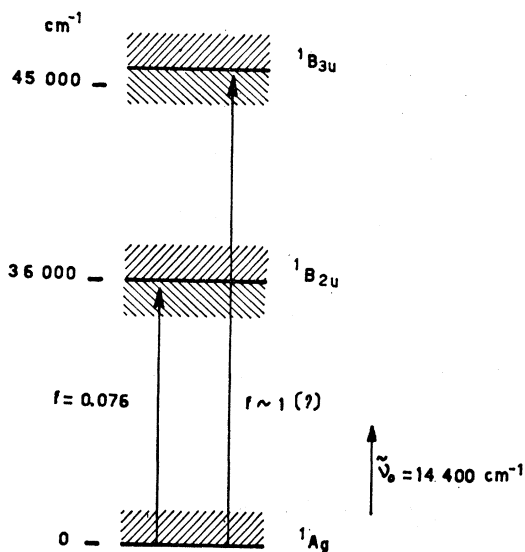


FIG. 2. Energy-band diagram of crystalline naphthalene.

${}^1B_{3u}$  transition in naphthalene (Fig. 2) with ruby laser light ( $\bar{\nu}_0 = 14\,400\text{ cm}^{-1}$ ). The experimental results of Pradère *et al.*<sup>2</sup> are

$$P_F = 2 \times 10^{-60} I_L^3 \quad (27a)$$

and

$$P_F = 1 \times 10^{-61} I_L^3 \quad (27b)$$

for anthracene and naphthalene, respectively. The experimental result of Singh and Bradley for naphthalene is

$$P_F = 1.5 \times 10^{-63} I_L^3. \quad (27c)$$

In Eqs. (27),  $P_F$  is the fluorescence in photons/cm<sup>3</sup> sec and  $I_L$  is the intensity of the incident radiation in photons/cm<sup>2</sup> sec. The uncertainty of all measurements is of an order of magnitude.

Indicating with indices 1 and 2 the intermediate virtual states,<sup>19</sup> we obtain from (20)

$$\begin{aligned} \bar{P}_{i \rightarrow f}^{(3)} = & 2^{-6} 3^{-1/2} \pi^{-4} (e^2/m\hbar)^3 c^{-10} (\Delta\omega)^2 f_{f2} f_{21} f_{1i} \\ & \times [(\bar{\nu}_{2i} - 2\bar{\nu}_0)^2 (\bar{\nu}_{i1} - \bar{\nu}_0)^2 \bar{\nu}_{f2} \bar{\nu}_{21} \bar{\nu}_{1i}]^{-1} g(3\omega_0 - \omega_c) I_L^3, \end{aligned}$$

where the  $f$  are the oscillator strengths. Introducing  $P_F$  and  $I_L$ , we get

$$\begin{aligned} P_F = & 2^{-1} 3^{-1/2} \pi (e^2/m)^3 c^{-7} f_{f2} f_{21} f_{1i} N_0 \bar{\nu}_0^3 \\ & \times [(\bar{\nu}_{2i} - 2\bar{\nu}_0)^2 (\bar{\nu}_{i1} - \bar{\nu}_0)^2 \bar{\nu}_{f2} \bar{\nu}_{21} \bar{\nu}_{1i}]^{-1} g(3\omega_0 - \omega_c) I_L^3, \quad (28) \end{aligned}$$

<sup>19</sup> Of the infinity of possible paths to pass from band  $i$  to band  $f$  by three steps, we consider only the  $i \rightarrow 1 \rightarrow 2 \rightarrow f$  path. We use the Hamiltonian (10) and we recall that F. V. Bunkin {Zh. Eksperim. i Teor. Fiz. 50, 1685 (1966) [English transl.: Soviet Phys.—JETP 23, 1121 (1966)]} proved that the use of the Hamiltonian in the form  $-(e/c)\mathbf{r} \cdot \partial \mathbf{A} / \partial t$  rather than  $-(e/mc)\mathbf{p} \cdot \mathbf{A}$  gives a better approximation if, among the intermediate levels with the oscillator strength not small, only the nearest levels to the initial state are taken into account. Actually, Bunkin proved this assertion only for two-photon transitions; yet it is reliable also for  $s$ -photon processes.

where  $N_0$  is the number of scattering centers per unit volume.

In anthracene, the molar extinction coefficient at  $\bar{\nu}_{fi} = 28\,300\text{ cm}^{-1}$  was found<sup>20</sup> to be  $\epsilon = 2 \times 10^3\text{ cm}^{-1} \times (\text{mole/liter})^{-1}$ , from which we get<sup>21</sup>  $f_{fi} g(3\omega_0 - \omega_c) = 2 \times 10^{-17}\text{ sec}$ . This result is in agreement with measurements in solution.<sup>22</sup> On the other hand, Wright<sup>23</sup> found the value  $K = 0.25$  for the absorption index, from which we get  $f_{fi} g(3\omega_0 - \omega_c) = 1.4 \times 10^{-16}\text{ sec}$ . For the  ${}^1A_g \rightarrow {}^1B_{3u} \rightarrow {}^1A_g \rightarrow {}^1B_{2u}$  path, using the two different  $f_{fi} g(3\omega_0 - \omega_c)$  values, we obtain  $P_F = 1.8 \times 10^{-62} \times I_L^3$  and  $P_F = 1.3 \times 10^{-61} I_L^3$ , respectively. These results compare rather well with (27a) considering the experimental uncertainties, and that moreover, the optical constants change from sample to sample.<sup>24</sup>

We wish now to consider three-photon absorption in naphthalene. Bree and Thirunamachandran<sup>25</sup> found  $\epsilon = 11 \times 10^3\text{ cm}^{-1} (\text{mole/liter})^{-1}$  at  $\bar{\nu}_{fi} = 43\,200\text{ cm}^{-1}$ , and so we have  $f_{fi} g(3\omega_0 - \omega_c) = 1.1 \times 10^{-16}\text{ sec}$ . For the  ${}^1A_g \rightarrow {}^1B_{2u} \rightarrow {}^1A_g \rightarrow {}^1B_{3u}$  path, Eq. (28) gives

$$P_F = 0.9 \times 10^{-63} I_L^3, \quad (29a)$$

in good agreement with (27c). To calculate the transition probability through the  ${}^1A_g \rightarrow {}^1B_{3u} \rightarrow {}^1A_g \rightarrow {}^1B_{3u}$  path we need to know  $f_{fi}$  and  $f_{fi} g(3\omega_0 - \omega_c)$ . Bree and Thirunamachandran<sup>25</sup> defined  $f_{\text{so1}} = f_a + f_b + f_c$ , but nevertheless they found experimentally  $f_{\text{so1}} = 1.21$ ,  $f_a \ll f_b$ ,  $f_b = 0.132$ , and  $f_c \approx 0$ . If we assume  $f_{fi} \approx 1$ , we have for the  ${}^1A_g \rightarrow {}^1B_{3u} \rightarrow {}^1A_g \rightarrow {}^1B_{3u}$  path

$$P_F = 1.7 \times 10^{-62} I_L^3. \quad (29b)$$

This result is in good agreement with both (27b) and (27c). On the other hand, if we choose  $f_{fi} = 0.132$ , we get for the same path

$$P_F = 0.3 \times 10^{-63} I_L^3. \quad (29c)$$

However, we must observe that (29a) and (29c) are of the same order of magnitude, and so if we choose  $f_{fi} = 0.132$  the contributions due to the different path can give rise to interferences.

Pradère *et al.*<sup>2</sup> studied in addition four-photon absorption in naphthalene; unfortunately for these transitions, the known data about the band structure are not sufficient to carry out reliable calculations.

<sup>20</sup> H. C. Wolf, Solid State Phys. 9, 52 (1959); Z. Naturforsch. 13a, 414 (1958).

<sup>21</sup> We recall that

$$\epsilon = 10^{-3} M \delta^{-1} \alpha = 2\pi^2 \times 10^{-3} e^2 (mc)^{-1} N_{\text{av}} f_{fi} g(\omega_{fi} - \omega_c),$$

where  $M$  is the molecular weight,  $\delta$  the density,  $\alpha$  the absorption coefficient, and  $N_{\text{av}}$  the Avogadro's number.

<sup>22</sup> W. L. Peticolas, J. P. Goldsborough, and K. E. Rieckhoff, Phys. Rev. Letters 10, 43 (1963). Actually the authors measured the absorption cross section at  $\bar{\nu} = 28\,800\text{ cm}^{-1}$ .

<sup>23</sup> W. H. Wright, J. Chem. Phys. 46, 2951 (1967). The author deduces the absorption index from refractive-index measurements.

<sup>24</sup> M. S. Brodin and S. I. Pekar, Zh. Eksperim. i Teor. Fiz. 38, 1910 (1960) [English transl.: Soviet Phys.—JETP 11, 1373 (1960)]; W. H. Wright J. Chem. Phys. 45, 874 (1966).

<sup>25</sup> A. Bree and T. Thirunamachandran, Mol. Phys. 5, 397 (1962).

APPENDIX

In this Appendix we evaluate the following integral:

$$\int dk_1 \int dk_2 \cdots \int dk_n (k_1 k_2 \cdots k_n)^{1/2} \times (k_{f_i} - k_1 - k_2 - \cdots - k_n)^{1/2} f(k_1; k_2; \cdots; k_n) \times \exp\{-l^2[(k_1 - k_0)^2 + (k_2 - k_0)^2 + \cdots + (k_n - k_0)^2 + (k_{f_i} - k_1 - k_2 - \cdots - k_n - k_0)^2]\}, \quad (A1)$$

where

$$l \gg k_0^{-1},$$

and  $f(k_1; k_2; \cdots; k_n)$  is a slowly variable function. We

can rewrite (A1) as

$$\int dk_1 \int dk_2 \cdots \int dk_n (k_1 k_2 \cdots k_n)^{1/2} \times (k_{f_i} - k_1 - k_2 - \cdots - k_n)^{1/2} f(k_1; k_2; \cdots; k_n) \times \exp(-l^2\{2[k_1 + \frac{1}{2}(\sum_{j=2}^n k_j) - \frac{1}{2}k_{f_i}]^2 + \frac{1}{2}[k_{f_i} - (\sum_{j=2}^n k_j) - 2k_0]^2 + [\sum_{j=2}^n (k_j - k_0)^2]\}).$$

Performing the integration over  $k_1$ , we have to a good approximation,

$$\frac{1}{l} \left(\frac{\pi}{2}\right)^{1/2} \int dk_2 \cdots \int dk_n (k_2 \cdots k_n)^{1/2} \left[\frac{1}{2}k_{f_i} - \frac{1}{2}(\sum_{j=2}^n k_j)\right] \exp(-l^2\{\frac{3}{2}[k_2 + \frac{1}{3}(\sum_{j=3}^n k_j) - \frac{1}{3}k_{f_i}]^2 + \frac{1}{3}[k_{f_i} - (\sum_{j=3}^n k_j) - 3k_0]^2 + [\sum_{j=3}^n (k_j - k_0)^2]\}) f\{k_1 = \frac{1}{2}[k_{f_i} - (\sum_{j=2}^n k_j)]; k_2; \cdots; k_n\}.$$

By performing likewise the integration over  $k_2$  and so on to the integration over  $k_{p-1}$ , we obtain

$$\pi^{1/2} l^{-p+1} p^{-1/2} \int dk_p \cdots \int dk_n (k_p \cdots k_n)^{1/2} \left[\frac{1}{p}k_{f_i} - \frac{1}{p}(\sum_{j=p}^n k_j)\right]^{1/2} \exp\left(-l^2\left\{\frac{p+1}{p}\left[k_p + \frac{1}{p+1}(\sum_{j=p+1}^n k_j) - \frac{1}{p+1}k_{f_i}\right]^2 + \frac{1}{p+1}[k_{f_i} - (\sum_{j=p+1}^n k_j) - (p+1)k_0]^2 + [\sum_{j=p+1}^n (k_j - k_0)^2]\right\}\right) f\left\{k_1 = k_2 = \cdots = k_{p-1} = \frac{1}{p}[k_{f_i} - (\sum_{j=p}^n k_j)]; k_p; \cdots; k_n\right\}.$$

When we perform all the integrations, this expression becomes

$$\pi^{n/2} l^{-n} (n+1)^{-1/2} f(k_1 = k_2 = \cdots = k_n = k_{f_i}/(n+1)) [k_{f_i}/(n+1)]^{1/2} \exp\{-[l^2/(n+1)][k_{f_i} - (n+1)k_0]^2\}. \quad (A2)$$

We observe that Eq. (18), after saturating the Dirac functions, can be written as a product of two (A1) integrals of order  $n = s - 1$ , where

$$\langle f | DR(\sum_{j=2}^n k_j) \cdots DR(k_n) D | i \rangle = f(k_1; k_2; \cdots; k_n).$$

Eq. (22) can be written introducing only one (A1) integral with

$$(k_1 k_2 \cdots k_n)^{1/2} (k_{f_i} - k_1 - k_2 - \cdots - k_n)^{1/2} |\langle f | \sum_{j=1}^n [DR(\sum_{\substack{i=1 \\ i \neq j}}^n k_i) \cdots DR(\sum_{\substack{i=j-1 \\ i \neq j}}^n k_i) \cdots D] | i \rangle|^2 = f(k_1; k_2; \cdots; k_n).$$

To suppose the  $f(k_1; k_2; \cdots; k_n)$  function to be slowly variable is well justified if no virtual levels are resonant.