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(Laser, Atomic and Molecular Physics)

PROPAGATION IN NON-LINEAR MEDIA:
REFRACTIVE INDEX IN NON-LINEAR MEDIA

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A.-S.F. Obada

**INTERNATIONAL
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PROPAGATION IN NON-LINEAR MEDIA:
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F.K. Faramawy   and   M.M. Abu Sitta

Mathematics Department, Faculty of Science, Al-Azhar University,
Nasr City, Cairo, Egypt

and

A.-S.F. Obada *

International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

A general theory of the effect of the electronic coupling between molecules on the response of the system as a whole to an external electromagnetic field is presented. The role of the non-linear response function for various physical quantities and their Fourier transformation is discussed. The non-linear susceptibilities to any rank for a denaturated system of particles are calculated. Also the non-linear response function for a coupled system is computed. A non-linear susceptibility for the electric dipole is obtained. Methods of the linear theory are developed to obtain the total non-linear refractive index.

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* Permanent address: Mathematics Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.

Preface

Introduction

The theory of the wave propagation in non-linear media can be developed along purely classical lines and the non-linear optical properties can be discussed along the same lines as the linear optical properties (Bloembergen)[1] .

Propagation effects are very important non-linear media because of the coherent nature of the exciting fields which in turn can generate coherent fields at other frequecies (Chemla)[2]. There are basically two classes of effects that can yield the desired refractive index   modulation . The first involves the response of a material to the local field strength (or intensity) . This phenomenon is called the Kerr effect . Examples of the physical processes that can be assigned to this category include orientation effects such as those that occur in glasses ,liquids ,or liquid crystal (Hellwarth)[3]. Saturation effects where atoms and/or molecules can have their refractive index modified owing to the local field intensity (Bullough)[4].

The second class of effects involves the response of a material to a non-**local** field. Physical processes relating to this phenomenon include responses for non-resonance four-wave non-linear optical interaction and thermal effect, where even the mild absorption of light can lead to a temperature gradient,which, through the temperature dependent refractive index can result in spatial modulation of the index (Martin and Hellwarth)[5].

To tackle the optical problems of an atomic (or molecular) system in the linear regime the linear response function has been introduced and used to calculate the refractive index of such a system in the electric-dipole approximations [6] and when magnetic-dipole contribution are taken into account [7]. When the system is supposed to compose of two-level atoms a non-linear response function has been calculated [8].

In this paper we pursue the investigation of the response of a medium to an electric field. The constituents of the medium are supposed to be atoms (or molecules) with multi-levels. We develop a non-linear response theory for this case.

After some preliminaries included in section 2 the results due to (Bloembergen)[1] for the non-linear susceptibilities and their generalizations for the isolated molecules in the case of harmonic generations are included in section 3.

In section 4 the Kubo formalism and the decorrelation approximation due to (Rhodes and Chase)[6] and (Obada et al)[7] are generalized developed and applied to obtain the polarizability of a system of particles coupled amongst themselves through an electro-magnetic field and subjected to an external electric field.

In section [5] we get a general expression for the non-linear polorization response function $\underline{\pi}(\underline{r} , \underline{r}' , t-t' , E)$.

In section 6 we consider the case of harmonic generation.

The refractive index of this medium is calculated by developing earlier methods in section 7.

2-Denaturated System

If we assume that the system of molecules and radiation has the Hamiltonian:

$$H = H_0 + H_{int}$$

where H_0 represents the Hamiltonian of the isolated molecules and the free field, while the interaction Hamiltonian density is described by (Obada et al)[7,8]

$$H_{int} = -\mu(r,t) \cdot E(r,t)$$

where $E(r,t)$ is a classical external electric field which has the representations:

$$E(r,t) = \int E(r,t) e^{i\omega t} d\omega$$

and the dipole moment:

$$\mu(r,t) = \sum_j \delta(r - r_j) \ \mu^j(t)$$

$$\mu^j(t) = \sum_s (\xi_s - r_j)$$

i.e $\mu(r,t)$ is the electric dipole moment of the system and $\mu^j(t)$ are the moments of the jth atom (or molecule) situated at r_j, whose electrons are at ξ_j.

All operators are taken in the interaction representation. In this picture the operator $Q(T)$ is:

$$Q(t) = e^{iH_0 t} \ Q(0) \ e^{-iH_0 t}$$

(Units $\hbar = c = 1$, and the notation of (Rhodes and Chase)[6] and (Obada et al)[7] is used).

Applying Kubo formalism for the perturbation and considering the terms of all orders in the external fields we arrive at the following expansion for the non-linear polarization:

$$\Delta\mu_i(r,t) = \langle \mu_i(r,t) \rangle - (|\mu_i(r,t)|)$$
$$= (i) \int\int_{-\infty}^{t} |[\mu_i(r,t), \mu_j(r_1,t_1)]|) \ E_j(r_1,t_1) \ dt_1 \ dr_1 + (i)^2 \int_{-\infty}^{t} dt_1 \int dr_1 \int_{-\infty}^{t_1} dt_2 \int dr_2 \int_{-\infty}^{t_2} dt_3 \int dr_3 \ \times$$
$$(|[[\mu_i(r,t), \mu_j(r_1,t_1)], \mu_k(r_2,t_2)]|) \ E_j(r_1,t_1) E_k(r_2,t_2)$$
$$+ \ldots + \ldots + \ldots +$$

$$((i) = \sqrt{-1} \ )$$

where $|\rangle$ is the exact state of the system and $|)$ is the state of the system before the switching on of the field interaction, repeated indices means summation over them. The integration over the space is taken over the volume of the system.

We can extend the temporal integration upper limit to $+\infty$ by introducing the θ-function and define the following polarizabilities:

$$_{i,j}(r,r_1;t-t_1) = (i)\theta(t-t_1) \ (|[\mu_i(r,t),\mu_j(r_1,t_1)]|)$$

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$$\pi_{i,jk}(r,r_1,r_2;t-t_1,t_1-t_2) = (i)^2\theta(t-t_1)\theta(t_1-t_2) \ (|[[\mu_i(r,t),\mu_j(r_1,t_1)],\mu_k(r_2,t_2)]|)$$

in general

$$\pi_{i,\alpha\ldots\beta}(r,r_1,\ldots,r_n,t-t_1,\ldots t_{n-1}-t_n)=(i)\theta(t-t_1)\ldots\ldots(i)\theta(t_{n-1}-t_n) \cdot$$

$$(|[\ldots[\ldots[\mu_i(r,t),\mu(r_1,t_1)]\ldots\ldots] \ \mu(r_n,t_n)]|) \cdot \qquad (2)$$

Thus we can write the first few members of the infinite series for $\Delta\mu(r,t)$ as follows:

$$\Delta\mu_i(r,t) = \int\int \pi^{(2)}_{i,}(\ r,r_1;t-t_1) \ E(r_1,t_1) \ dr_1 \ dt_1 \ +$$

$$\int\int\int\int \{ \ \pi^{(3)}_{i,\alpha\beta}(r,r_1,r_2;t-t_1,t_1-t_2)E(r_1,t_1)E(r_2,t_2)\}dr_1 \ dt_1 \ dr_2 \ dt_2 \ +$$

$$\int\int\int\int\int\int \pi^{(4)}_{i,\alpha\beta\gamma}(r,r_1,r_2,r_3;t-t_1,t_1-t_2,t_2-t_3) \ E_\alpha(r_1,t_1) \ E_\beta(r_2,t_2) \ E_\gamma(r_3,t_3) \times$$

$$\times \ dr_1 \ dt_1 \ dr_2 \ dt_2 \ dr_3 \ dt_3$$

$$+\ldots\ldots + \ldots\ldots \qquad (3)$$

We may write this infinite series in the following symbolic form:

$$\Delta \langle | \mu | \rangle = \pi^*(1-E)^{-1}E \qquad (4)$$

where:

$$\pi^* \cdot E = \pi_{i,\alpha} E = \pi^{(2)}_{i,\alpha}(r,r_1,t-t_1) \ E_\alpha(r_1,t_1)$$

and in general;

$$(\pi^* :E\ldots\ldots E)_i = \pi_{i,\alpha\ldots\ldots\beta} \underbrace{E\ldots\ldots E}_{n} = \pi_{i,\alpha\ldots\beta}(r,r_1\ldots\ldots r_n,t-t_1,\ldots\ldots,t_{n-1}-t_n)$$

$$E(r_1,t_1) \ldots\ldots\ldots E(r_n,t_n) \qquad (5)$$

We take ensemble average (see ref.4) to get the polarization field $P(r,t)$ as follows

$$P(r,t) = \Delta \langle | \mu(r,t) | \rangle$$

In what follows the ensemble average is supposed to be taken.

Thus the non-linear polarization of the denaturated system in electric field which may be defined through:

$$P_{NL} = P - P_L = \pi_{NL} \cdot E$$

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where

$$\Pi_{NL} \cdot \underset{\sim}{E} = \Pi^*(1-\underset{\sim}{E})^{-1}\underset{\sim}{E} - \overset{(2)}{\Pi}\underset{\sim}{E} \tag{6}$$

where the symbolic forms are explained in (2) and (5).

In what follows we calculate these susceptibilities.

3-Non-linear susceptibilities

We assume that the system is composed of isolated atoms (or molecules) and the interaction amongst them is neglected (i.e assume a denaturated system). There is no overlap between the wave-functions of the different atoms (or molecules).Thus the spatial integrations break up into integrals over volumes surrounding the particles.

To get the non-linear susceptibility we take the Fourier transformation of equation (3) with respect to (t).Hence we shall take $\tau_1 = t - t_1 \ldots \ldots \tau_n = t_{n-1} - t_n$.

For the second term in equation (3) we can easily show:

$$\int dr_1 \int dr_2 \int dt_1 \int dt_2 \ \overset{(3)}{\pi}_{i,\alpha\beta}(r,r_1,r_2,t-t_1,t_1-t_2) \ \underset{\sim}{E}(r_1,t_1) \ \underset{\sim}{E}(r_2,t_2)$$

$$= \int dr_1 \int dr_2 \int\int \sum_j e^3 \sum_{s,k} \Big[(x_i^j)^{os}(x^j)^{sk}(x^j)^{ko} (\omega_1+\omega_2-\omega_{so})^{-1}(\omega_2-\omega_{ko})^{-1}$$

$$- (x^j)^{os}(x_i^j)^{sk}(x^j)^{ko} (\omega_2-\omega_{ko})^{-1}(\omega_1+\omega_2-\omega_{sk})^{-1} - (x^j)^{os}(x_i^j)^{sk}(x^j)^{ko}(\omega_2+\omega_{so})^{-1}(\omega_1+\omega_2-\omega_{sk})^{-1}$$

$$+ (x^j)^{os}(x^j)^{sk}(x_i^j)^{ko}(\omega_1+\omega_2-\omega_{so})^{-1}(\omega_2-\omega_{ko})^{-1} \Big] e^{-i(\omega_1+\omega_2)t} \ \underset{\sim}{E}(r_1,\omega_1)\underset{\beta}{E}(r_2,\omega_2) \times$$

$$\times \ \delta(r-r_j) \delta(r-r_1) \ \delta(r_1-r_2) \ d\omega_1 \ d\omega_2$$

$$= \int\int \sum_j \overset{j(3)}{\alpha}_{i,\alpha\beta}(\omega_3=\omega_1+\omega_2;\omega_1,\omega_2) \ e^{-i\omega_3 t} \ \delta(r-r_j) \ \underset{\sim}{E}(r,\omega_1)\underset{\beta}{E}(r,\omega_2) \ d\omega_1 \ d\omega_2$$

where $\overset{j(3)}{\alpha}$ is a third rank tensor describing the higher order polarizability of the j th molecule.

The appearance of the δ-function over the integrals is due to the localization of the atomic (or molecular) wave-functions and assuming that the particles are far apart.

We ought to remind ourselves here,that ensemble averages are taken ,thus instead of $\sum_j \overset{j}{\alpha} \delta(r-r_j)$ its average should appear which is $N\alpha$ where (N) is the molecular density when the medium is composed of a single constituent.

If we take $\omega_1 = \omega_2 = \omega$ (second harmonic generation) and take the fourier transformations on (t) with frequency equal 2ω.we finally get:(for simplicity we assume here that μ has only a component along x-direction)

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$$\overset{(3)}{\alpha}(\omega_3=2\omega;\omega,\omega) = e^3 \sum_{s,k} (x^j)^{os}(x^j)^{sk}(x^j)^{ko} \Big[(2\omega-\omega_{so})^{-1}(\omega-\omega_{ko})^{-1} -$$

$$- (\omega+\omega_{so})^{-1}(\omega-\omega_{ko})^{-1} + (2\omega+\omega_{so})^{-1}(\omega+\omega_{ko})^{-1} \Big]$$

By the same methods one can show:(dropping the particle's index j)

$$\overset{(4)}{\alpha}(\omega_4=3\omega;\omega,\omega,\omega) = e^4 \sum_{s,k,\ell} x^{os} x^{sk} x^{k\ell} x^{\ell o} (3\omega-\omega_{so})^{-1}(2\omega-\omega_{ko})^{-1}(\omega-\omega_{\ell o})^{-1}$$

$$-(\omega+\omega_{so})^{-1}(2\omega-\omega_{ko})^{-1}(\omega-\omega_{\ell o})^{-1} + (\omega-\omega_{so})^{-1}(\omega-\omega_{ko})^{-1}(\omega+\omega_{\ell o})^{-1}$$

$$- (3\omega+\omega_{so})^{-1}(2\omega+\omega_{ko})^{-1}(\omega+\omega_{\ell o})^{-1} \tag{7a}$$

This is the result due to (Bloembergen and Pershan)[9].

Also we get the following 5th and 6th order non-linear polarizablities:

$$\overset{(5)}{\alpha}(4\omega;\omega,\omega,\omega) = e^5 \sum_{s,k,\ell,m} x^{os} x^{sk} x^{k\ell} x^{\ell m} x^{mo} \Big[(4\omega-\omega_{so})^{-1}(3\omega-\omega_{ko})^{-1}(2\omega-\omega_{\ell o})^{-1} \times$$

$$\times (\omega-\omega_{mo})^{-1} - (\omega+\omega_{so})^{-1}(3\omega-\omega_{ko})^{-1}(2\omega-\omega_{\ell o})^{-1}(\omega-\omega_{mo})^{-1}$$

$$+ (\omega+\omega_{so})^{-1}(2\omega+\omega_{ko})^{-1}(2\omega-\omega_{\ell o})^{-1}(\omega-\omega_{mo})^{-1} +$$

$$- (\omega+\omega_{so})^{-1}(3\omega+\omega_{ko})^{-1}(2\omega+\omega_{\ell o})^{-1}(\omega+\omega_{mo})^{-1} +$$

$$+ (4\omega+\omega_{so})^{-1}(3\omega+\omega_{ko})^{-1}(2\omega+\omega_{\ell o})^{-1}(\omega+\omega_{mo})^{-1} \Big] \tag{7b}$$

And

$$\overset{(6)}{\alpha}(5\omega;\omega,\omega,\omega,\omega,\omega) = e^6 \sum_{s,k,\ell,m,n} x^{os} x^{sk} x^{k\ell} x^{\ell m} x^{mn} x^{no} \times$$

$$\times \Big[(5\omega-\omega_{so})^{-1}(4\omega-\omega_{ko})^{-1}(3\omega-\omega_{\ell o})^{-1}(2\omega-\omega_{mo})^{-1}(\omega-\omega_{no})^{-1}$$

$$- (\omega+\omega_{so})^{-1}(4\omega-\omega_{ko})^{-1}(3\omega-\omega_{\ell o})^{-1}(2\omega-\omega_{mo})^{-1}(\omega-\omega_{no})^{-1}$$

$$+ (\omega+\omega_{so})^{-1}(2\omega+\omega_{ko})^{-1}(3\omega-\omega_{\ell o})^{-1}(2\omega-\omega_{mo})^{-1}(\omega-\omega_{no})^{-1}$$

$$- (\omega-\omega_{so})^{-1}(2\omega-\omega_{ko})^{-1}(3\omega+\omega_{\ell o})^{-1}(2\omega+\omega_{mo})^{-1}(\omega+\omega_{no})^{-1}$$

$$+ (\omega-\omega_{so})^{-1}(4\omega+\omega_{ko})^{-1}(3\omega+\omega_{\ell o})^{-1}(2\omega+\omega_{mo})^{-1}(\omega+\omega_{no})^{-1}$$

$$- (5\omega+\omega_{so})^{-1}(4\omega+\omega_{ko})^{-1}(3\omega+\omega_{\ell o})^{-1}(2\omega+\omega_{mo})^{-1}(\omega+\omega_{no})^{-1} \Big] \tag{7c}$$

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We would like to mention the assumption that have been used so far:

1- $\mu^{sk} = \mu^{ks}$ which means real wave-function and conservation of parity.

2- we have taken incoming frequencies to get second harmonic generation for $\alpha^{(3)}(2\omega)$, third harmonic generation for $\alpha^{(4)}(3\omega)$ and so on.

Now we look at the preceding polarizabilities and define:

$$\beta_j^+(n\omega) = (\omega + \omega_{1,o})^{-1}(2\omega + \omega_{2,o})^{-1}\ldots\ldots(j\omega + \omega_{j,o})^{-1}((n-j)\omega - \omega_{j+1,o})^{-1}\ldots\ldots(\omega - \omega_{n,o})^{-1}$$

(8a)

$$\beta_j^+(n\omega) = (\omega - \omega_{1,o})^{-1}(2\omega - \omega_{2,o})^{-1}\ldots\ldots(j\omega - \omega_{j,o})^{-1}((n-j)\omega - \omega_{j+1,o})^{-1}\ldots\ldots(\omega - \omega_{n,o})^{-1}$$

(8b)

Using equations(7) and (8)we can put the nth term $\alpha(n\omega)$ in the following form.

$$\alpha^{(n+1)}(n\omega) = e^n(\sum_{s\ldots n} x^{os} x^{sk}\ldots x^{no}\left[\sum_{j=0}^{(n/2)-1}(-1)^j(\beta_j^+(n\omega)+\beta_j^-(n\omega))+(-1)^{n/2}\beta_{\frac{n}{2}}^+(n\omega)\right]$$

(for even n) .(9)

while for odd (n) the expression assumes the following form:

$$\alpha^{(n+1)}(n\omega) = e^n(\sum_{s\ldots h} x^{os}x^{sk}\ldots x^{no}\left[\sum_{j=0}^{(n-1)/2}(\beta_j^+(n\omega)-\beta_j^-(n\omega))\right]$$

(10)

Where we use $\omega_{1,o} = \omega_{so}$, $\omega_{2,o} = \omega_{ko}$;... and so on, with $\omega_{ss'} = E_s - E_{s'}$.

Also $\alpha(n\omega) = \alpha(n\omega; \underbrace{\omega,\omega,\omega,\ldots\ldots\omega}_{n})$ is a tensor of rank (n +1), in general.

Equations (9) and (10) are the main results of this section. It is noted that when we put n = 1 we get the linear molecular susceptibility. If we take n=2,and n=3 ,we get the Bloembergen's results for the non-linear susceptibilities.

According to the previous results we can write the non-linear susceptibility for the denaturated system as follows:

$$P(\omega)= N\{(1!)\alpha^{(2)}(\omega).E(\omega)+ (2!)\alpha^{(3)}(2\omega;\omega',\omega):E(\omega')E(\omega') +$$

$$(3!)\alpha^{(4)}(3\omega;\omega'',\omega'',\omega'')\vdots E(\omega'')E(\omega'')E(\omega'') +\ldots\ldots+\ldots \}$$

(*)

where N is the molecular density and the field frequencies are such that:

$$\omega = \omega' + \omega' = \omega'' + \omega'' + \omega'' = \ldots$$

The physical meaning of the above equation is the following:

The electromagnetic fields derive distortion of the electric charges which may oscillate at any combination of the (ω')and they in turn radiate at the corresponding frequencies (Chemla)[6]. The factor (3!) for example in equation (*)appears because of the fact that there are 6 combinations of the form: $E_i(\omega'')E_j(\omega'')E_k(\omega'')$ in the product:

$$\alpha^{(4)}_{n,ijk}(\omega,\omega'',\omega'',\omega'',)E_i(\omega'')E_j(\omega'')E_k(\omega'')$$

where the indices i, j and k label the cartesian components of the field ; in the belief that the tensors are symmetric in the cartesian indices (Chemla)[6].

In what follows we will consider the case of a coupled system.

4. Non-linear Polarizability Function for a Coupled System

In the last section we assume that the particles are isolated from each other and they projected to the external impinging field only.In this section we relax this restriction We assume that the particles interact amongst themselves this interaction is taken the form:(Obada et al)[7,8]

$$H_{int}(r,t) = -\mu(r,t).(e(r,t) + E(r,t))$$

where $e(r,t)$ is a second-quantized electric field operator which represents the interaction between the constituents of the system and $E(r,t)$ is the classical external field.

In what follows we define the non-linear response function to all orders in the applied external field . To perform this ,we use the Kubo formalism to get an expansion for the expression $\Delta\langle|\mu(r,t)|\rangle$ in all orders of the external field . Thus, to the first order of the external field (E) we obtain the linear response (Rhodes and Chase)[6] and (Obada et al)[7], in the second order of the external field (E E) we obtain the non-linear response of the second order , etc. . Applying Kubo formalism for the perturbation and developing the decoupling scheme developed earlier[5,7]we arrive at the following expression by assuming that the system was a denaturated system at t = -∞:

$$\underline{\mu}(\underline{r},t) = (i) \int d\underline{r}_1 \int_{-\infty}^{t} dt_1 (\mid [\underline{\mu},\underline{\mu}_1] \cdot (\underline{e}_1 + \underline{E}_1) \mid)$$

$$+ (i)^2 \int d\underline{r}_1 \int_{-\infty}^{t} dt_1 \int d\underline{r}_2 \int_{-\infty}^{t_1} dt_2 \Big[(\mid [\ulcorner \underline{\mu},\underline{\mu}_1 \urcorner,\underline{\mu}_2] (\underline{e}_1 + \underline{E}_1) (\underline{e}_2 + \underline{E}_2) \mid) +$$

$$+ (\mid [\underline{\mu},\underline{\mu}_1] \ulcorner (\underline{e}_1 + \underline{E}_1), (\underline{e}_2 + \underline{E}_2) \urcorner \underline{\mu}_2 \mid) \Big] + (i)^3 \int d\underline{r}_1 \int_{-\infty}^{t} dt_1 \int d\underline{r}_2 \int_{-\infty}^{t_1} dt_2 \int d\underline{r}_3 \int_{-\infty}^{t_2} dt_3 \, X$$

$$X \Big[(\mid [[[\underline{\mu},\underline{\mu}_1],\underline{\mu}_2],\underline{\mu}_3] (\underline{e}_3 + \underline{E}_3) (\underline{e}_2 + \underline{E}_2) (\underline{e}_1 + \underline{E}_1) \mid) +$$

$$+ (\mid [[\underline{\mu},\underline{\mu}_1],\underline{\mu}_2] [(\underline{e}_2 + \underline{E}_2) (\underline{e}_1 + \underline{E}_1), (\underline{e}_3 + \underline{E}_3)] \underline{\mu}_3 \mid) +$$

$$+ (\mid [\underline{\mu},\underline{\mu}_1] [(\underline{e}_1 + \underline{E}_1), (\underline{e}_2 + \underline{E}_2)] [\underline{\mu}_2,\underline{\mu}_3] (\underline{e}_3 + \underline{E}_3) \mid) \Big] +$$

$$+ (i)^4 \int d\underline{r}_1 \int_{-\infty}^{t} dt_1 \int d\underline{r}_2 \int_{-\infty}^{t_1} dt_2 \int d\underline{r}_3 \int_{-\infty}^{t_2} dt_3 \int d\underline{r}_4 \int_{-\infty}^{t_3} dt_4 \quad X$$

$$\Big[(\mid [[[[\underline{\mu},\underline{\mu}_1],\underline{\mu}_2],\underline{\mu}_3],\underline{\mu}_4] (\underline{e}_4 + \underline{E}_4) (\underline{e}_3 + \underline{E}_3) (\underline{e}_2 + \underline{E}_2) (\underline{e}_1 + \underline{E}_1) \mid)$$

$$+ (\mid [[[\underline{\mu},\underline{\mu}_1],\underline{\mu}_2],\underline{\mu}_3] [(\underline{e}_3 + \underline{E}_3) (\underline{e}_2 + \underline{E}_2) (\underline{e}_1 + \underline{E}_1), (\underline{e}_4 + \underline{E}_4)] \underline{\mu}_4 \mid)$$

$$+ (\mid [[\underline{\mu},\underline{\mu}_1],\underline{\mu}_2] [(\underline{e}_2 + \underline{E}_2)(\underline{e}_1 + \underline{E}_1), (\underline{e}_3 + \underline{E}_3)] [\underline{\mu}_3,\underline{\mu}_4] (\underline{e}_4 + \underline{E}_4) \mid)$$

$$+ (\mid [\underline{\mu},\underline{\mu}_1] [(\underline{e}_1 + \underline{E}_1), (\underline{e}_2 + \underline{E}_2)] [[\underline{\mu}_2,\underline{\mu}_3],\underline{\mu}_4] (\underline{e}_4 + \underline{E}_4) (\underline{e}_3 + \underline{E}_3) \mid)$$

$$+ (\mid [\underline{\mu},\underline{\mu}_1] [(\underline{e}_1 + \underline{E}_1), (\underline{e}_2 + \underline{E}_2)] [\underline{\mu}_2,\underline{\mu}_3] [(\underline{e}_3 + \underline{E}_3), (\underline{e}_4 + \underline{E}_4)] \underline{\mu}_4 \mid) \Big] +$$

$$+ \ldots \, \ldots + \ldots\ldots\ldots + \, \ldots \tag{11}$$

where we use $\underline{\mu}_i$, $\underline{e}_i$ and $\underline{E}_i$ to symbolize $\underline{\mu}(\underline{r}_i,t_i)$, $\underline{e}(\underline{r}_i,t_i)$, and $\underline{E}(\underline{r}_i,t_i)$ respectively The state $\mid)$ is the state of the free field and isolated particles. The field commutator $\ulcorner \underline{e}_i, \underline{e}_j \urcorner$ is a C-number. The operators $\underline{e}$ and $\underline{\mu}$ are assumed to commute and $[\underline{e}, \underline{E}] = 0$ because $\underline{E}$ is a C-number.

We suppose a decorrelation scheme similar to that used earlier[7,8] to be applicable. The scheme amounts to replacing $\ulcorner \ldots\ldots [[\underline{\mu}, \underline{\mu}_1], \underline{\mu}_2] \ldots\ldots \urcorner$ by its expectation value. Further the following assumptions are taken into consideration:

a)- $(\mid \underline{\mu} \mid) \longrightarrow 0$ and $(\mid \text{odd number of } \underline{e} \mid) \longrightarrow 0$

b)- We neglect the overlap between the isolated molecular wave-function. Thus the commutator nests involving the atomic operators become local, as seen in the calculation of the non-linear suceptibilities of section (3).

c)- We neglect $(\mid \underline{e}(\underline{r},t) \, \underline{e}(\underline{r}_1,t_1) \ldots\ldots \mid)$ (i.e) we neglect the self field contributions.

We introduce the following field propagators:

$$F^{(3)}_{bc,d} (\underline{r}_1,\underline{r}_2,\underline{r}_3; t_1,t_2,t_3) = (i) \theta(t_1 - t_2) \theta(t_2 - t_3) \quad X$$

$$X \, [(\underline{E}_c(\underline{r}_2,t_2) + \underline{e}_c(\underline{r}_2,t_2))(\underline{E}_b(\underline{r}_1,t_1) + \underline{e}_b(\underline{r}_1,t_1)), (\underline{E}_d(\underline{r}_3,t_3) + \underline{e}_d(\underline{r}_3,t_3))] =$$

$$= (i) \theta(t_1 - t_3) \underline{E}_c(\underline{r}_2,t_2) [\underline{e}_b(\underline{r}_1,t_1), \underline{e}_d(\underline{r}_3,t_3)] +$$

$$+ (i) \theta(t_2 - t_3) \underline{E}_b(\underline{r}_1,t_1) [\underline{e}_c(\underline{r}_2,t_2), \underline{e}_d(\underline{r}_3,t_3)] =$$

$$= \underline{E}_c(\underline{r}_2,t_2) F^{(2)}_{b,d}(\underline{r}_1,\underline{r}_3; t_1 - t_3) + \underline{E}_b(\underline{r}_1,t_1) F^{(2)}_{c,d}(\underline{r}_2,\underline{r}_3; t_2 - t_3) \tag{12}$$

where,

$$F^{(2)}_{a,b}(\underline{r},\underline{r}'; t - t') = (i) \theta(t - t') [\underline{e}_a(\underline{r},t), \underline{e}_b(\underline{r}',t')]$$

Because of the assumption (b) the external fields are evaluated at the same point. In general:

$$F^{(n)}_{ab\ldots n-1, n} (\underline{r}_1,\underline{r}_2,\ldots \underline{r}_n; t_1, t_2 \ldots t_n) = [(\underline{E}_1 + \underline{e}_1) \ldots (\underline{E}_{n-1} + \underline{e}_{n-1}), (\underline{E}_n + \underline{e}_n)] \tag{13}$$

The fourier transformation of the electric field commutator $[\underline{e}_a(\underline{r},t), \underline{e}_b(\underline{r}',t')]$ at different space-time points (Power)[10] is:

$$F^{(2)}_{a,b}(\underline{r},\underline{r}';\omega) = \Big[(-\underline{\nabla}_r \underline{\nabla}_{r'} + k_o^2 \, \underline{U}) \frac{e^{ik_o \mid \underline{r} - \underline{r}' \mid}}{\mid \underline{r} - \underline{r}' \mid} \Big]_{a,b} \tag{14}$$

where $\underline{\underline{U}}$ is the second rank unit tensor.

According to all these considerations ,and taking the definition of $\pi^{(2)}$,$\pi^{(3)}$,.. as before we can write equation (11) in the following form (after omitting all integrations and arguments)

$$\underline{P}_{L+NL} = \Delta \langle | \underline{u} | \rangle = \pi^{(2)} \cdot \underline{E} + \pi^{(3)} : \underline{E}\,\underline{E} + \pi^{(4)} \vdots \underline{E}\,\underline{E}\,\underline{E} + \cdots + \cdots$$

$$+ \pi^{(2)}\, F^{(2)} \pi^{(2)} \cdot \underline{E} + \pi^{(2)}\, F^{(2)} \pi^{(2)}\, F^{(2)} \pi^{(2)} \cdot \underline{E} + \cdots$$

$$+ \pi^{(2)}\, F^{(2)} \pi^{(3)} : \underline{E}\,\underline{E} + \pi^{(2)}\, F^{(2)} \pi^{(4)} \vdots \underline{E}\,\underline{E}\,\underline{E} + \cdots + \cdots$$

$$+ \pi^{(3)}\, F^{(3)} \pi^{(2)} \cdot \underline{E} + \pi^{(3)}\, F^{(3)} \pi^{(3)} : \underline{E}\,\underline{E} + \pi^{(3)}\, F^{(3)} \pi^{(4)} \vdots \underline{E}\,\underline{E}\,\underline{E} + \cdots$$

$$+ \pi^{(2)}\, F^{(2)} \pi^{(3)}\, F^{(3)} \pi^{(4)} \vdots \underline{E}\,\underline{E}\,\underline{E} + \cdots + \cdots$$

$$+ \cdots + \cdots \tag{15}$$

(i.e)

$$\underline{P}_{L+NL} = (1 - R)^{-1}\, \underline{S} = \underline{S} + R\, \underline{P}_{L+NL} \tag{16}$$

Where ;

$$\underline{S} = \pi^{(2)} \cdot \underline{E} + \pi^{(3)} : \underline{E}\,\underline{E} + \pi^{(4)} \vdots \underline{E}\,\underline{E}\,\underline{E} + \pi^{(5)} \vdots \underline{E}\,\underline{E}\,\underline{E}\,\underline{E} + \cdots + \cdots \tag{17}$$

and

$$R = \pi^{(2)}\, F^{(2)} + \pi^{(3)}\, F^{(3)} + \pi^{(4)}\, F^{(4)} + \pi^{(5)}\, F^{(5)} + \cdots + \cdots + \cdots \tag{18}$$

Equation (16) gives linear and non-linear polarization response in all orders of the external field. Thus we can write the non-linear polarizability only on the form:

$$\underline{P}_{NL} = (1 - R)^{-1}\, \underline{S} - \pi^{(2)} (1 - F^{(2)} \pi^{(2)})^{-1} \cdot \underline{E} \tag{19}$$

The series $\underline{S}$ only in the above equation gives all previous results (Chemla)[2] and (Fisher)[11].
We develop this formula in the following section.

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5- Polarization Non-linear Response Function

We can define the linear and non-linear response function by using the adiabatic switching through the fomula:

$$\Delta \langle | \underline{u}\,(\underline{r},t) | \rangle = \int dr' \int dt'\; \underline{\underline{\pi}}\,(\underline{r},\underline{r}';t - t',\underline{E})\, \underline{E}\,(\underline{r}',t') \tag{20}$$

Thus ,if we write the external field $\underline{E}(\underline{r}',t')$ in the form:

$$\underline{E}(\underline{r}',t') = \delta(\underline{r} - \underline{r}')\, \delta(t - t') \tag{21}$$

Then the function $\underline{\underline{\pi}}(\underline{r},\underline{r}';t-t',\underline{E})$ is the dipole moment of the system due to this elctric field . By using equations(15), (20) and (21)we can write the non-linear response function for a coupled system in interaction with an electric field on the following form:

$$\underline{\underline{\pi}}_{L+NL} = (1 - R)^{-1}\, \underline{S} = \underline{S} + R\, \underline{\underline{\pi}}_{L+NL} \tag{22}$$

(the integrations and arguments have been omitted) where,

$$\underline{S} = \underline{S} \cdot \underline{E}$$

(i.e)

$$\underline{S} = \pi^{(2)} + \pi^{(3)} \cdot \underline{E} + \pi^{(4)} : \underline{E}\,\underline{E} + \cdots + \cdots \tag{23}$$

Thus we can write the non-linear response function only for the coupled system in the form:

$$\underline{\underline{\pi}}_{NL} = (1 - R)^{-1}\, \underline{S} - \pi^{(2)} (1 - F^{(2)} \pi^{(2)})^{-1} \tag{24}$$

The second part of the right hand side in equation (24) is the linear response function which had been obtained by (Obada et al)[7] .The dependence of the frequecy (ω) is given in what follows.

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6- Non-linear Susceptibility for a Coupled System

To get the corresponding susceptibilities for the coupled system we take the fourier transformation of equation (15) with respect to time (t).The integration, $\left\{\int\int_V \underline{F}\ (\underline{r},\underline{r}';\omega)\ \underline{P}(\underline{r}';\omega)\ d\underline{r}'\right\}$ evaluated by using the results due to (Bullough)[4] in section (7).

Let us take for example the following term from equation (15): (carrying out all integration over the space of molecules and using the fact that $\alpha^{(n)}$ connecting different molecules is zero)

$$\int dt_1 \int dt_2 \int dt_3 \int dt_4 \int dt_5 \int dt_6 \quad X$$

$$\sum_{n,n'} {}^n\alpha_{i,kjl}(\tau_1,\tau_2,\tau_3)\ F_{ljk,m}(\underline{r}_n,\underline{r}_n,\underline{r}_n,\underline{r}_{n'};t_1,t_2,t_3,t_4)\ {}^{n'}\alpha_{m,su}(\tau_5,\tau_6)E_u(\underline{r}_{n'},t_5)\ E_s(\underline{r}_{n'},t_6)$$

Indices n , n' now label molecules since the integrations were taken over a small volume arround the particle. The summation is implied over repeated indices.

We can now change all integrations on $\tau_1,\tau_2,\tau_3,\tau_4,\tau_5,\tau_6$ instead of t_1,t_2,t_3,t_4, t_5,t_6 respectively,then the time limits are extend to infinity since $\theta(\tau) = 0$ for $\tau < 0$, and $\theta(\tau) = 1$ for $\tau > 0$ .If we take $\omega_1=\omega_2=\omega_3=2\omega$,and $\omega_5=\omega_6=\omega$ one can easily show that the corresponding susceptibility for this term takes the form:

$$\sum_{n,n'} {}^n\alpha\ (6\omega;2\omega,2\omega,2\omega)\left[F(2\omega)_{ljk,m}\right]_{nnn,n'} {}^{n'}\alpha\ (2\omega;\omega,\omega)\ E_{n'}(\omega)\ E_{n'}(\omega)$$

where

$$\left[F(2\omega)_{\ell jk,m}\right]_{nnn,n'} = E(2\omega)_{n,\ell}\ E(2\omega)_{n,j}\left[F(2\omega)_{k,m}\right]_{n,n'} + E(2\omega)_{n,\ell}\ E(2\omega)_{n,k}\left[F(2\omega)_{j,m}\right]_{n,n'} +$$

$$+ E(2\omega)_{n,j}\ E(2\omega)_{n,k}\left[F(2\omega)_{\ell,m}\right]_{n,n'} = 3\ E(2\omega)_{n,\ell}\ E(2\omega)_{n,k}\left[F(2\omega)_{j,m}\right]_{n,n'}$$

where the indices ℓ,k,j and m label the cartesian components of the fields $\underline{E}(t_1)$, $\underline{E}(t_2)$, $\underline{E}(t_3)$ and $\underline{E}(t_4)$; and the susceptibilities are taken symmetric.

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In general

$$F^{(n)}_{1\ 2\ 3\ \ldots n-1,n}(\omega') = \left[\sum_{i=1}^{n-1}\ (\prod_{\substack{j=1\\ j\neq i}}^{n-2} E_j(\omega'))\ F^{(2)}_{1,n}(\omega')\right]$$

Also one can show that the corresponding susceptibility of term like:

$$\int dt_1 \int dt_2 \int dt_3 \int dt_4 \ldots\ldots\ldots \int dt_{11}$$

$$\alpha_{a,bcde}(\tau_1,\tau_2,\tau_3,\tau_4)\ F_{edcb,f}(t_1,t_2,t_3,t_4,t_5)\ \alpha_{f,gh}(\tau_6,\tau_7)\ F_{hg,i}(t_6,t_7,t_8)\ \alpha_{i,jkl}(\tau_9,\tau_{10},\tau_{11})\ X$$

$$E_j(t_9)\ E_k(t_{10})\ E_l(t_{11})\ .$$

is;

$$\alpha_{a,bcde}\ (24\omega;6\omega,6\omega,6\omega,6\omega)\ F_{edcb,f}\ (6\omega)\ \alpha_{f,gh}\ (6\omega;3\omega,3\omega)\ F_{hg,i}\ (3\omega)\ \alpha_{i,jkl}(3\omega;\omega,\omega,\omega)\ E_j(\omega)\ E_k(\omega)\ E_l(\omega)\ .$$

Since we take $\omega_1=\omega_2=\omega_3=\omega_4=6\omega$; $\omega_6=\omega_7=3\omega$ and $\omega_9=\omega_{10}=\omega_{11}=\omega$. And we write, F dropping the $\underline{r}$ labeling which will be understood.

Thus one can show that the corresponding susceptibility for equation (16) takes form:

$$\underline{P}_{L+NL}(\omega,\ \underline{E}) = \sum_{n=1}^{\infty} (n!)\ \alpha^{(n+1)}(\omega;\underbrace{\frac{\omega}{n},\frac{\omega}{n},\ \frac{\omega}{n},\ \ldots\ldots\frac{\omega}{n}}_{n})\ E^{n-1}(\frac{\omega}{n})\left[E(\frac{\omega}{n})+\underline{F}(\frac{\omega}{n})\ \underline{P}_{L+NL}(\frac{\omega}{n})\right]$$

$$(25)$$

By using the same technique one can show that the corresponding susceptibility for the non-linear response function; $\underline{\underline{\Pi}}_{L+NL} = (1 - R)^{-1}\ \underline{\underline{S}}$ is:

$$\underline{\underline{\Pi}}(\omega,\underline{E}) = \underline{\underline{\Pi}}_{L+NL}(\omega,\underline{E}) = \sum_{n=1}^{\infty} (n!)\ \alpha^{(n+1)}(\omega;\underbrace{\frac{\omega}{n}\ \frac{\omega}{n}\frac{\omega}{n}\ldots\ldots\ \frac{\omega}{n}}_{n})\ E^{n-1}(\frac{\omega}{n})\left[1+\underline{F}(\frac{\omega}{n})\ \underline{\underline{\Pi}}(\frac{\omega}{n},\underline{E})\right]$$

$$(26)$$

Equations (25) and (26) are the main results of this section.

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It is clear that if we take $n=1$ we obtain the linear susceptibility which had been obtained by (Obada et al)[7].

We may look at the non-linear susceptibility and non-linear response of the field. By using the same technique ,and take all previous assumptions, one can show:

$$\Delta \langle |\underline{E}| \rangle = \underline{F} \ (1- R)^{-1} \ \underline{S} \tag{27}$$

The corresponding susceptibility takes the following form:

$$\Delta \langle \underline{E}(\omega) \rangle = \underline{F}(\omega) \ \underline{P}_{L+NL}(\omega) \tag{28}$$

where $\underline{P}_{L+NL}(\omega)$ is obtained from equation (25)

Let us now dicuss the total refractive index in the non-linear medium using the previous results . This is done in the next section.

7- Refractive Index in Non-linear Media:

We assume that $\underline{P}_{L+NL}$ satisfies the sourceless equation (i.e);

$$(\nabla^2 + K_p^2) \ \underline{P}_{L+NL} = 0 \tag{29}$$

Also

$$\underline{F}(\underline{r},\underline{r}'; \frac{\omega}{n}) = (\nabla \nabla + K^2 \underline{U}) \ \frac{e^{iK|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|}$$

where,

$$K = \frac{\omega}{n} = \frac{k_o}{n} \tag{30}$$

And;

$$\underline{P}_{L+NL}(\underline{r},\omega) = \sum_{n=1}^{\infty} (n!) \ \alpha^{(n+1)}(\omega;\frac{\omega}{n}, \frac{\omega}{n},\dots \frac{\omega}{n}) \ E^{n-1}(\underline{r},\frac{\omega}{n}) \left[E(\underline{r},\frac{\omega}{n}) + \int \underline{F}(\underline{r},\underline{r}';\frac{\omega}{n}) \ \underline{P}_{L+NL}(\underline{r}';\frac{\omega}{n})d\underline{r}' \right]$$

We assume that $\underline{E}(\underline{r},\frac{\omega}{n})$ satisfies Maxwell's equation in vacuo (i.e)

$$\nabla \cdot \underline{E}(\underline{r}, K) = 0 \tag{31}$$

and,

$$(\nabla^2 + K^2) \ \underline{E}(\underline{r}, K) = 0 \tag{32}$$

Therefore ,by using the results due to (Bullough)[4] which are essentially Ewald-Oseen theory (see Born and Walf)[12] ,one can easily show:

$$\underline{P}_{L+NL}(\underline{r}) = \sum_{n=1}^{\infty} (n!) \ \alpha^{(n+1)}(\omega;\frac{\omega}{n},\frac{\omega}{n},\dots \frac{\omega}{n}) \ E^{n-1}(\underline{r},K) \left[E(\underline{r},K)+ \frac{4 (\nabla_r \nabla_r + K^2 \underline{U})}{K_p^2 - K^2} + \frac{4}{3} \underline{P}_{L+NL}(\underline{r}) + \frac{(\nabla_r \nabla_r + K^2)}{K_p^2 - K^2} \underline{Z}(\underline{r},K) \right] \tag{33}$$

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where

$$\underline{Z}(\underline{r},K) = \int_s \underline{P}_{L+NL}(\underline{r}) \ (\nabla \frac{e^{iK|\underline{r}-\underline{r}'|}}{\underline{r}-\underline{r}'} \cdot d\underline{s}) - (\frac{e^{iK|\underline{r}-\underline{r}'|}}{\underline{r}-\underline{r}'}d\underline{s} \cdot \nabla) \ \underline{P}_{L+NL}(\underline{r}) \tag{34}$$

which is an integration over the surface of the system.

Since $\underline{E}$ and $\underline{Z}$ satisfy equation (32) and $\underline{P}_{L+NL}$ satisfies equation (29), thus equation (33) breaks up into two equations which are:

$$\underline{P}_{L+NL}(\underline{r}) = \sum_{n=1}^{\infty} (n!) \ \alpha^{(n+1)}(\omega;\frac{\omega}{n},\frac{\omega}{n},\dots \frac{\omega}{n})E^{n-1}(\underline{r},K) \left[\frac{4\pi(\nabla \nabla + K^2 \underline{U})}{K_p^2 - K^2} + \frac{4\pi}{3} \right] \underline{P}_{L+NL}(\underline{r}) \tag{35}$$

and,

$$\underline{E}(\underline{r},K) + \underline{Z}(\underline{r}, K) = 0 \tag{36}$$

If we assume that:

$$\underline{P}_{L+NL} = \underline{P}^L_{L+NL} + \underline{P}^T_{L+NL}$$

where,

$$\nabla \cdot \underline{P}^T_{L+NL} = 0 \qquad ; \qquad \nabla \wedge \underline{P}^L_{L+NL} = 0$$

We assume that $\underline{P}^T_{L+NL}$ and $\underline{P}^L_{L+NL}$ separately satisfy equation (29) ,we readily find that equation (35) again splits into:

$$\underline{P}^L_{L+NL}(\underline{r}) = \sum_{n=1}^{\infty} (n!) \ \alpha^{(n+1)}(\omega;\frac{\omega}{n},\frac{\omega}{n},\dots \frac{\omega}{n}) \ E^{n-1}(\underline{r},K) \left[\frac{4\pi}{3} + \frac{4\pi(\nabla^2 + K^2)}{K_p^2 - K^2} \right] \underline{P}^L_{L+NL}(\underline{r})$$

and,
$$\dots \dots (37)$$

$$\underline{P}^T_{L+NL}(\underline{r}) = \sum_{n=1}^{\infty} (n!) \ \alpha^{(n+1)}(\omega;\frac{\omega}{n},\frac{\omega}{n},\dots \dots \frac{\omega}{n}) \ E^{n-1}(\underline{r}, K) \left[\frac{4\pi}{3} + \frac{4\pi K^2}{K_p^2 - K^2} \right] \underline{P}^T_{L+NL}(\underline{r}) \tag{38}$$

From equation (38) we have:

$$\frac{K_p^2 - K^2}{K_p^2 + 2K^2} = \frac{4\pi}{3} \sum_{n=1}^{\infty} (n!) \ \alpha^{(n+1)}(\omega;\frac{\omega}{n},\dots \dots,\frac{\omega}{n}) \ E^{n-1}(\frac{\omega}{n}) \tag{39}$$

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The refractive index $m = |\underline{K}_p|/|\underline{K}|$; $|\underline{K}| = k_o / n$, therefore equation (39) gives:

$$\frac{(K_p^2 / K^2) - 1}{(K_p^2 / K^2) + 2} = \frac{4\pi}{3} \sum_{n=1}^{\infty} (n!) \alpha^{(n+1)}(\omega; \frac{\omega}{n}, \frac{\omega}{n}, \ldots \frac{\omega}{n}) E^{n-1}(\frac{\omega}{n})$$

(i.e)

$$\frac{n^2 m^2 - 1}{n^2 m^2 + 2} = \frac{4\pi}{3} \sum_{n=1}^{\infty} (n!) \alpha^{(n+1)}(\omega; \frac{\omega}{n}, \frac{\omega}{n}, \ldots \frac{\omega}{n}) E^{n-1}(\frac{\omega}{n}) \qquad (40)$$

It is clear that the above equation is a generalized form of the result due to (Bullough)[4] and (Fisher)[11].

Also equation (40) gives Kerr-effects (third order polarizability in external field or fourth rank susceptibility tensor) (Fisher)[11] as follows.

We put n m ≉ 1 and take n = 1 , n = 3 only in the R. H. S. of equation (40) ,we have:

$$\frac{(n m)^2 - 1}{3} = \frac{4\pi}{3} \left[(1!) \alpha^{(2)} + (3!) \alpha^{(4)} E^2 \right]$$

then

$$n m = 1 + 2\pi \alpha^{(2)} + 12\pi \alpha^{(4)} E^2$$

or

$$m = m_o + m_2 \langle E^2 \rangle \qquad (41)$$

where

$n_o = 1 + 2\pi \alpha^{(2)}$ is the linear refractive index ; $m_2 = 12\pi \alpha^{(4)}$ is the non-linear refractive index ,and m is the total refractive index and the brackets $\langle \ \rangle$ denote a temporal average.

Equation (41) coincide exactly with the result due to (Fisher)[11].Also if we substitute from (29) into equation (37) we get:

$$P_{L+NL}^L (\underline{r}) = - \frac{8\pi}{3} \sum_{n=1}^{\infty} (n!) \alpha^{(n+1)}(\omega; \frac{\omega}{n}, \frac{\omega}{n}, \ldots \frac{\omega}{n}) E^{n-1}(\frac{\omega}{n}) P_{L+NL}^L (\underline{r}) \qquad (42)$$

The above equation is the generalized form of the linear equation due to (Bullough)[4].

Therefore we can say that the non-linear equations (40) and (42) are more general than those presented earlier (Bullough)[4],(Fisher)[11].

The result $P_{L+NL} = (1 - R) \underline{S} = \underline{S} + R P_{L+NL}$ gives linear and non-linear polarization response for a coupled system of molecules in all order of the external field.

The first series ($\underline{S}$) in this equation gives all previous results for the denaturated system of molecules (Bloembergen[1], Chemla[2], Fisher[11]). The other parts in this equation ($R\underline{S}$, $RR\underline{S}$,...) may be though of as internal field cotribution.

It is to be noted that the linear and non-linear polarization field gives rise to the internal electric field. For example the term ($\pi^{(4)} F^{(4)} \pi^{(3)} : E E$) shows that the non-linear polarization field $\pi^{(3)} : E E$ gives rise to a non-linear electric polarization field carried by the propagator $F^{(4)}$. These field in turn induce an electric polarization field through the fourth rank tensor $\pi^{(4)}$. Also if we take the linear part in the external field only from the non-linear response function $\pi_{L+NL} = (1 - R)^{-1} \underline{S} = \underline{S} + R \pi_{L+NL}$ we have the linear response function which had been obtained by (Obada et al)[7].If we put the electric field propagators equal zero in this equation (denaturated system) we obtain the results due to (Bloembergen[1], Murayan[13a,b]).

The results based on the equation:

$$P_{L+NL}(\omega) = \sum_{n=1}^{\infty} (n!) \alpha^{(n+1)}(\omega; \frac{\omega}{n}, \frac{\omega}{n}, \frac{\omega}{n}, \ldots \frac{\omega}{n}) E^{n-1}(\frac{\omega}{n}) E(\frac{\omega}{n}) + F(\frac{\omega}{n}) P_{L+NL}(\frac{\omega}{n})$$

are more general than those obtained earlier ,if we put n = 1 we get the linear susceptibility for a coupled system (Obada et al)[7]. Also if we take the first few terms (and put the field propagators equal zero) in second and third order in the external field we get all previous results for denaturated system (Bloembergen and Pershan[9],Chemla,[2] Fisher[11]).

In section(7) we devoloped the results due to (Bullough)[4] to get a general form for the refractive index in non-linear media (equation 40). this equation is more general than those presented earlier in the case of the linear theory (Bullough)[4]. The results quoted by Fisher)[11] and (Chemla)[2] are a special case from equation(40) as we had shown.

Through this paper, basic approximations have been used:

1– The general decorrelation approximation which generalizes that due to (Rhodes and Chase)[6] partially decouples , the motion of the electrons on different molecules .

2– The molecular seprability approximation , since we deal with the molecular system at zero temperature in which the indivdual molecular units are sufficiently separated so that the overlap effects can be neglected. .

3– We neglect the self fields of the molecules . The first approximation in its simplest form is necessary to put the theory in the closed form and it is difficult to assess .

4– We assume that the medium is lossless , nondispersive , and uniform . Under these conditions the susceptibility tensor $\alpha^{(n)}$ are symmetric tensor (Hillery and Mlodinow)[14].

5– Through this article we assume the dipole approximation since we neglect the spatial dispersion of the molecular susceptibility $\alpha^{(n)}$,(i.e) the polarization at a point is completely determined by the value of the field at the same point (Agranovich and Ginzburg)[15] ,also $\alpha^{(n)}$ connecting different moleculs is zero .

6– The electric fied is supposed to be described by a C–number external probe and a second quantized field that describes the internal field .

7– We ignore terms on the form $(|\mu[[\ldots[\mu_1,\mu_2]\ldots]]|)$ so that stark effects as well as self energies are ignored .

Finally we would like to mention that we obtained the general form of the susceptibility for a coupled system (equation 23) on the basis of very general principles namely ; the principle of time invariance which states that , the properties of the medium are independent of time ; the causality principle according to which $\underline{P}(t)$ depends only on the fields for time earlier than (t) ,and the reality principle which ensures that the response of the medium to a real driving field , is real (Butcher[16], Flytzanis[17]) .

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