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SYMMETRY PROPERTIES OF SECOND ORDER HYPERPOLARIZABILITIES

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Abstract Time-reversal symmetry property of a second order nonlinear optical hyperpolarizability is examined in terms of the Manley-Rowe power relation to find relationship to the overall permutation symmetry. An extended symmetry relation is discovered reducing the independent number of the hyperpolarizability tensor components describing the second order nonlinear optical processes. Experimental implications are discussed.

1. Introduction

Understanding the molecular structure of a second order nonlinear optical material is important in designing molecules with a high optical nonlinearity as well as in developing new structures for a nonlinear optical process. The optical response of a molecule is highly related to the point group symmetry properties of molecular structure. For example, the absence of centrosymmetry is prerequisite to the non-vanishing second order nonlinear optical response. Second order nonlinear optical process itself, on the other hand, possesses a certain symmetry property independent of the molecular symmetry. In a second harmonic generation, for instance, two incident photons with the identical optical frequency combine to generate one photon with the frequency twice of the incident photon frequency. Here two incident photons are degenerate in the sense that the order of the interaction of each photon is irrelevant to generating the second harmonics. This is one example of symmetry property occurring in second order nonlinear optical processes, independent of the molecular symmetry. In a non-dissipative system, there exist two important symmetries satisfied by microscopic nonlinear optical hyperpolarizabilities $\gamma^{(n)}_{ijk\cdots}(\omega_\sigma;\omega_1,\omega_2,\cdots)$ with $\omega_\sigma = -\omega_1 - \omega_2 - \cdots$. One is the overall permutation symmetry (OPS), and the other is the time-reversal symmetry (TRS). In this paper we examine these symmetry properties of second order nonlinear optical hyperpolarizabilities and find a

relationship between those symmetries elucidating the implication of the relationship in experimental measurements. In Section 2 we discuss the time reversal symmetry in a second order nonlinear optical process. In Section 3 the overall permutation symmetry is studied in relation to the Manley-Rowe power relation holding in a non-dissipative regime of nonlinear optical process. By examining the microscopic photon creation and annihilation process the time reversal symmetry is found to be implied in derivation of the Manley-Rowe power relation in Section 4. This leads to the extended symmetry property of second order hyperpolarizabilities, which is explained in Section 5. Experimental implications of the extended symmetry property are discussed in Section 6.

2. Time-Reversal Symmetry (TRS)

TRS is a fundamental symmetry in various fields of physics, which is related to the change of the sign of time in a physical process.[1] Electromagnetic interaction is time-reversal invariant. Hence, in a nonlinear optical process, one of electromagnetic interactions, TRS holds rigorously. In the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\Psi(\vec{x},t)}{\partial t} = H\Psi(\vec{x},t) \tag{1}$$

the time reversal operation is simply taking a complex conjugate of the equation. Under the time-reversal the sign of the vector potential $\vec{A}(\vec{x},t)$ appearing in the minimal coupling is changed, i.e., the sign of a magnetic field is changed, while the sign of an electric field remains unchanged.[2] Microscopic hyperpolarizabilities behave differently under the time-reversal operation (T) depending on the vector fields involved. In the electric dipolar (E1) approximation, only the electric fields are responsible for the induced nonlinear polarization.

$$p_i^{\omega_\sigma} = \gamma_{ijk\cdots}^{(n)}(\omega_\sigma;\omega_1,\omega_2,\cdots)E_j^{\omega_1}E_k^{\omega_2}\cdots \tag{2}$$

Therefore under the time-reversal operation there is no change of sign. All we need to do is to take the complex conjugate of the hyperpolarizability.

$$T[\gamma_{ijk\cdots}^{(n)}(\omega_\sigma;\omega_1,\omega_2,\cdots)] = \gamma_{ijk\cdots}^{(n)*}(\omega_\sigma;\omega_1,\omega_2,\cdots) \tag{3}$$

Now the reality condition of optical polarizabilities in the time domain provides the following relation between the complex conjugates of $\gamma_{ijk\cdots}^{(n)}(\omega_\sigma;\omega_1,\omega_2,\cdots)$.

$$\gamma_{ijk\cdots}^{(n)*}(\omega_\sigma;\omega_1,\omega_2,\cdots) = \gamma_{ijk\cdots}^{(n)}(-\omega_\sigma;-\omega_1,-\omega_2,-\cdots) \tag{4}$$

That is, taking the complex conjugate is identical to changing the sign of optical frequencies. Therefore, when TRS holds, the hyperpolarizabilities satisfy a simple relation.

$$\gamma^{(n)}_{ijk\cdots}(\omega_\sigma;\omega_1,\omega_2,\cdots) = \gamma^{(n)}_{ijk\cdots}(-\omega_\sigma;-\omega_1,-\omega_2,-\cdots) \tag{5}$$

3. Manley-Rowe Power Relation and Overall Permutation Symmetry (OPS)

Let's look at the Manley-Rowe power relation. In a non-dissipative system, the nonlinear interaction between the optical fields and the electronic charges in molecules results in the generation of harmonics. When monochromatic waves with two incommensurate frequencies ω_1 and ω_2 are incident on a nonlinear optical medium, the optical nonlinearity gives rise to waves with the combination frequencies $\omega_{mn} = m\omega_1 + n\omega_2$ (m & n are integers). The conversion of frequencies through a nonlinear optical process causes the change of N_{mn} (the number of photons with the frequency ω_{mn}) in time with the total energy conserved.

$$\frac{dU}{dt} = \hbar\omega_1 \sum_{m,n} m\frac{dN_{mn}}{dt} + \hbar\omega_2 \sum_{m,n} n\frac{dN_{mn}}{dt} = 0 \tag{6}$$

Since ω_1 and ω_2 are incommensurate and the changes in the photon numbers are integers, each summation in Eq.(6) vanishes identically. In terms of the intensities of the radiations, U_{mn}, this condition gives the well-known Manley-Rowe power relation.

$$\sum_{m,n} \frac{m}{\omega_{mn}}\frac{dU_{mn}}{dt} = 0, \quad \sum_{m,n} \frac{n}{\omega_{mn}}\frac{dU_{mn}}{dt} = 0 \tag{7}$$

The Manley-Rowe relation describes the exchange of power between the wave fields interacting in a purely reactive, non-dissipative nonlinear optical medium. From the Manley-Rowe power relation OPS can be derived easily by considering the field energies of each frequency involved in the nonlinear process. In the simple case of a sum-frequency generation from ω_1 and ω_2, the substitution of the field energies into the Manley-Rowe relation, Eq.(7), leads to OPS.[3]

$$\begin{aligned} \beta_{ijk}(\omega_\sigma;\omega_1,\omega_2) &= \beta_{jik}(\omega_1;\omega_\sigma,\omega_2) \\ &= \beta_{kji}(\omega_2;\omega_1,\omega_\sigma) \end{aligned} \tag{8}$$

where $\beta_{ijk}(\omega_\sigma;\omega_1,\omega_2)$ is the second order nonlinear optical hyperpolarizability relating the induced polarization $p_i^{\omega_\sigma}$ with the incident fields $E_j^{\omega_1}$ and $E_k^{\omega_2}$, i.e.,

$$p_i^{\omega_\sigma} = \beta_{ijk}(\omega_\sigma;\omega_1,\omega_2)E_j^{\omega_1}E_k^{\omega_2} \tag{9}$$

OPS (Eq.(8)) states that the microscopic nonlinear optical polarizabilities are invariant under a simultaneous permutation of the index pairs among (i,ω_σ), (j,ω_1), (k,ω_2), $\cdots$. Originally the invariance of $\gamma^{(n)}_{ijk\ldots}(\omega_\sigma;\omega_1,\omega_2,\cdots)$ under a permutation of tensor indices $i,j,k,\cdots$ without permuting the corresponding optical frequencies $\omega_\sigma,\omega_1,\omega_2\cdots$ was discovered by Kleinman.[4] While the Kleinman symmetry is true only in the off-resonance, dispersionless regime, OPS holds in the regime where the frequency dispersions are present. Hence, OPS is a higher symmetry than Kleinman's, and was first noted by Armstrong *et al.*[5] from the examination of the explicit quantum mechanical expression of $\gamma^{(n)}_{ijk\ldots}(\omega_\sigma;\omega_1,\omega_2,\cdots)$. Even though OPS is obvious from the explicit form of hyperpolarizabilities, we note that it is related to the Manley-Rowe power relation which has an important physical significance.

4. Time Reversal Symmetry and Manley-Rowe Power Relation

Now let's look at the assumptions behind the Manley-Rowe relation. In a microscopic process of the generation of harmonics, two incident waves with incommensurate frequencies ω_1 and ω_2 are assumed to generate waves with harmonic frequencies ω_{mn}. In a closer look, we will see that a harmonics generation from two photons with incommensurate frequencies is a time-reversal invariant process. The time-reversed process for a sum-frequency generation,

$$\omega_{mn} = m\omega_1 + n\omega_2, \tag{10}$$

is a splitting of a photon with frequency ω_{mn} into photons with frequencies ω_1 and ω_2. This splitting process can be viewed as a sum-frequency generation of photons with frequencies ω_2 from two incident photons ω_{mn} and $-\omega_1$.

$$\begin{aligned} \omega_{kl} &= k\omega_{mn} + l(-\omega_1) \\ &= k\omega_{mn} - l\omega_1 \end{aligned} \tag{11}$$

We note that the frequency $\omega_{mn} = m\omega_1 + n\omega_2$ is *always incommensurate* with ω_1 for non-zero integers m and n. Eq.(11) shows, then, the time-reversed process is another harmonics generation from photons with incommensurate frequencies. In fact, the new frequency ω_{kl} generated in the time-reversed process can be ω_2 when a suitable choice of the integers k and l is made for given m and n. That is, by substituting ω_{mn} into Eq.(11) we obtain

$$\omega_{kl} = (km - l)\omega_1 + kn\omega_2 = kn\omega_2, \quad \text{for} \quad km = l \tag{12}$$

Therefore, TRS holds for a harmonics generation process. From the implication of TRS in the assumptions for the Manley-Rowe relation employed in the derivation of OPS (Eq.(8)), it is evident that OPS is invariant under the operation of time-reversal. In other words, OPS in a non-dissipative medium is a consequence of TRS.

5. Relationship between OPS and TRS

Now by use of OPS and the hermitian property of the dipole operator $\vec{x}$, it can be shown explicitly that the nonlinear optical hyperpolarizability satisfies TRS from the quantum mechanical expression. Here we adopt the expression where OPS is explicitly stated by introducing the total symmetrization operator S_T permuting the pair of indices (i,ω_σ), (j,ω_1), (k,ω_2).[6] In the sum-frequency generation, for example,

$$\begin{aligned}
&\beta_{ijk}(\omega_\sigma;\omega_1,\omega_2)\\
&= \frac{e^3}{4\hbar^2}S_T\sum_{m,n} < g \mid x_i \mid m >< m \mid x_j \mid n >< n \mid x_k \mid g > \frac{1}{(\omega_{mg}+\omega_\sigma)(\omega_{ng}-\omega_2)}\\
&= \frac{e^3}{4\hbar^2}S_T\sum_{m,n} < g \mid x_k^\dagger \mid m >< m \mid x_j^\dagger \mid n >< n \mid x_i^\dagger \mid g > \frac{1}{(\omega_{ng}+\omega_\sigma)(\omega_{mg}-\omega_2)}\\
&= \frac{e^3}{4\hbar^2}S_T\sum_{m,n} < g \mid x_k \mid m >< m \mid x_j \mid n >< n \mid x_i \mid g > \frac{1}{(\omega_{mg}-\omega_2)(\omega_{ng}+\omega_\sigma)}\\
&= \frac{e^3}{4\hbar^2}S_T\sum_{m,n} < g \mid x_i \mid m >< m \mid x_j \mid n >< n \mid x_k \mid g > \frac{1}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}+\omega_2)}\\
&= \beta_{ijk}(-\omega_\sigma;-\omega_1,-\omega_2) \qquad (13)
\end{aligned}$$

where the dummy variables m,n are exchanged, and OPS operation is applied on the index pairs of (i,ω_σ) and (k,ω_2). Again, we find that TRS is implied in OPS for a non-dissipative optical medium. In the case of a sum-frequency generation, as a particular example of Eq.(5), we find OPS relation of Eq.(8) should be extended to include TRS.

$$\begin{aligned}
\beta_{ijk}(\omega_\sigma;\omega_1,\omega_2) &= \beta_{ijk}(-\omega_\sigma;-\omega_1,-\omega_2)\\
&= \beta_{jik}(\omega_1;\omega_\sigma,\omega_2)\\
&= \beta_{kji}(\omega_2;\omega_1,\omega_\sigma) \qquad (14)
\end{aligned}$$

Usually TRS is treated separately from OPS, and OPS and TRS are known as two independent symmetries of a non-dissipative optical system.[6] For instance, TRS

was invoked to show the absence of macroscopic electro-optic effects in an optically active isotropic liquids, distinguished from OPS.[7][8] But we find that OPS is a consequence of TRS.

6. Discussions

OPS alone was examined experimentally in a KDP crystal by looking at an electro-optic (EO) effect and an optical rectification (RECT) process.[9]

$$\begin{aligned} & \beta_{ijk}^{EO}(-\omega;0,\omega) = \beta_{ijk}(\omega_\sigma = -\omega;0,\omega) \\ = \; & \beta_{jik}(0;\omega_\sigma = -\omega,\omega) = \beta_{jik}^{RECT}(0;-\omega,\omega). \end{aligned} \tag{15}$$

It is found that the same parameter governs two different processes of the EO effect and the optical rectification process. Now the extended symmtery relation Eq.(14) predicts that there exists a new relation between two different nonlinear optical processes when degenerate photons are involved.[10] Interestingly, we find that

$$\begin{aligned} & \beta_{ijk}(\omega_\sigma = -2\omega;\omega,\omega) \\ = \; & \beta_{jik}(\omega;\omega_\sigma = -2\omega,\omega) \\ = \; & \beta_{jik}(-\omega;-\omega_\sigma = 2\omega,-\omega). \end{aligned} \tag{16}$$

That is, a second harmonic generation $\beta_{ijk}(-2\omega;\omega,\omega)$ and a difference frequency generation $\beta_{jik}(-\omega;2\omega,-\omega)$ are governed by the same parameter. This can be examined relatively easily in a non-dissipative regime of an inorganic crystal such as a KDP crystal. Additionally, the relation, Eq.(16), reduces the number of independent nonlinear optical susceptibility tensor components, allowing an efficient design of phase matching nonlinear optical crystals for example. The extended symmerty relation, similar to Eq.(14), can also be found without any difficulty in the third and higher order processes, which will be useful in relating the apparently different nonlinear optical processes. In summary, we have shown that the overall permutation symmetry of the microscopic nonlinear optical hyperpolarizabilities $\gamma_{ijk\ldots}^{(n)}(\omega_\sigma;\omega_1,\omega_2,\cdots)$ in a non-dissipative optical medium is a consequence of the time-reversal symmetry, as indicated from the time-reversal invariant property of microscopic harmonics generation process in the Manley-Rowe power relation. The overall permutation and time-reversal symmetry should be considered as one extended symmetry holding in a non-dissipative optical medium, rather than two independent symmetries. The relation between the overall permuation and time-reversal symmetry reduces the number

of independent nonlinear optical susceptibility tensor components. In a second order sum-frequency generation process in a non-dissipative regime, it is predicted that a second-harmonic generation and a difference-frequency generation are governed by the same parameter.

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