Relationship between the overall permutation and time-reversal symmetries in the nonlinear optical hyperpolarizabilities

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The overall-permutation-symmetry property of the nonlinear optical hyperpolarizabilities in a nondissipative medium is examined to find that the time-reversal symmetry is already assumed in the Manley-Rowe power relation, a basic relation adopted in the derivation of the overall permutation symmetry. This indicates that the overall permutation symmetry is a consequence of the time-reversal symmetry. The quantum-mechanical expression of hyperpolarizability is shown to satisfy both the overall permutation and the time-reversal symmetry explicitly. From the extended symmetry relation, it is predicted that second-harmonic generation and difference-frequency generation, two different nonlinear optical processes, are governed by the same parameter.

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Symmetry properties of nonlinear optical hyperpolarizabilities are of importance in distinguishing each microscopic nonlinear optical process and understanding the relations between different nonlinear optical processes. Spatial symmetry of the optical medium, for example, determines the nonvanishing components of the macroscopic nonlinear optical susceptibility tensor $\chi^{(n)}_{\alpha\beta\gamma\ldots}(\omega_\sigma;\omega_1,\omega_2,\ldots)$ with $\omega_\sigma=-\omega_1-\omega_2-\cdots$. In a nondissipative system, in addition to the spatial symmetry, there exist two important symmetries satisfied by the microscopic nonlinear optical hyperpolarizabilities $\gamma^{(n)}_{ijk\ldots}(\omega_\sigma;\omega_1,\omega_2,\ldots)$ with $\omega_\sigma=-\omega_1-\omega_2-\cdots$. One is the overall permutation symmetry (OPS), and the other is the time-reversal symmetry (TRS). OPS states that the microscopic nonlinear optical polarizabilities are invariant under a simultaneous permutation of the index pairs among (i,ω_σ), (j,ω_1), $(k,\omega_2),\ldots$. Originally the invariance of $\gamma^{(n)}_{ijk\ldots}(\omega_\sigma;\omega_1,\omega_2,\ldots)$ under a permutation of tensor indices $i,j,k,\ldots$ without permuting the corresponding optical frequencies $\omega_\sigma,\omega_1,\omega_2,\ldots$ was discovered by Kleinman [1]. By considering the Kleinman symmetry of a nonlinear optical susceptibility in a given medium, the physical mechanism for each nonlinear optical process can be identified. OPS is a higher symmetry than Kleinman's, and was first noted by Armstrong *et al.* [2] from the examination of the explicit quantum-mechanical expression of $\gamma^{(n)}_{ijk\ldots}(\omega_\sigma;\omega_1,\omega_2,\ldots)$. Even though OPS is obvious from the explicit form of hyperpolarizabilities, it is related to the Manley-Rowe power relation, which has an important physical significance. More importantly, OPS can be *derived* from the Manley-Rowe power relation [3]. On the other hand, TRS, a more fundamental symmetry than OPS, is related to the change of the sign of time in a physical process [4]. Electromagnetic interaction is a time-reversal invariant. Hence, in a nonlinear optical process, one of the electromagnetic interactions, TRS holds rigorously. Usually TRS is treated separately from OPS, and OPS and TRS are known as two independent symmetries of a nondissipative optical system [5]. For instance, TRS was invoked to show the absence of macroscopic electro-optic effects in optically active isotropic liquids, distinguished from OPS [6,7]. In this Brief Report, we investigate the assumptions made in the derivation of OPS, and find that OPS is a consequence of TRS. We also prove that explicitly by examining the quantum-mechanical expression of the nonlinear optical hyperpolarizability. Furthermore, from the extended symmetry relation, we discover that a second-harmonic generation and a difference-frequency generation, two seemingly unrelated nonlinear optical processes, are governed by the same parameter.

Let us look at the Manley-Rowe power relation briefly. In a nondissipative 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 and 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:

$$\frac{dU}{dt}=\hbar\omega_1\sum_{m,n}m\frac{dN_{mn}}{dt}+\hbar\omega_2\sum_{m,n}n\frac{dN_{mn}}{dt}=0\ . \tag{1}$$

Since ω_1 and ω_2 are incommensurate and the changes in the photon numbers are integers, each summation in Eq. (1) vanishes identically. In terms of the intensities of the radiations U_{mn} this condition gives the well-known Manley-Rowe power relation

$$\sum_{m,n}\frac{m}{\omega_{mn}}\frac{dU_{mn}}{dt}=0\ ,\quad \sum_{m,n}\frac{n}{\omega_{mn}}\frac{dU_{mn}}{dt}=0\ . \tag{2}$$

The Manley-Rowe relation describes the exchange of power between the wave fields interacting in a purely reactive, nondissipative 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. (2), leads to OPS [3]

$$\beta_{ijk}(\omega_\sigma;\omega_1,\omega_2)=\beta_{jik}(\omega_1;\omega_\sigma,\omega_2)=\beta_{kji}(\omega_2;\omega_1,\omega_\sigma) , \tag{3}$$

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.,

$$p_i^{\omega_\sigma}=\beta_{ijk}(\omega_\sigma;\omega_1,\omega_2)E_j^{\omega_1}E_k^{\omega_2} . \tag{4}$$

Now let us 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

$$\omega_{mn}=m\omega_1+n\omega_2 , \tag{5}$$

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 $-\omega_1$:

$$\omega_{kl}=k\omega_{mn}+l(-\omega_1)=k\omega_{mn}-l\omega_1 . \tag{6}$$

We note that the frequency $\omega_{mn}=n\omega_1+n\omega_2$ is *always incommensurate* with ω_1 for nonzero integers m and n. Equation (6) shows, then, the time-reversed process is another harmonics generation from photon 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. (6), we obtain

$$\omega_{kl}=(km-l)\omega_1+kn\omega_2=kn\omega_2 \quad \text{for } km=l . \tag{7}$$

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. (3)], it is evident that OPS is invariant under the operation of time reversal. In other words, OPS in a nondissipative medium is a consequence of TRS.

Under the time reversal the sign of the vector potential $\mathbf{A}(\mathbf{x},t)$ 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 [8]. 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:

$$p_i^{\omega_\sigma}=\gamma_{ijk\ldots}^{(n)}(\omega_\sigma;\omega_1,\omega_2,\ldots)E_j^{\omega_1}E_k^{\omega_2}\cdots . \tag{8}$$

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

$$T[\gamma_{ijk\ldots}^{(n)}(\omega_\sigma;\omega_1,\omega_2,\ldots)] =\gamma_{ijk\ldots}^{(n)*}(\omega_\sigma;\omega_1,\omega_2,\ldots) . \tag{9}$$

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

$$\gamma_{ijk\ldots}^{(n)*}(\omega_\sigma;\omega_1,\omega_2,\ldots) =\gamma_{ijk\ldots}^{(n)}(-\omega_\sigma;-\omega_1,-\omega_2,\ldots) . \tag{10}$$

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

$$\gamma_{ijk\ldots}^{(n)}(\omega_\sigma;\omega_1,\omega_2,\ldots) =\gamma_{ijk\ldots}^{(n)}(-\omega_\sigma;-\omega_1,-\omega_2,\ldots) . \tag{11}$$

In the case of a sum-frequency generation, as a particular example of Eq. (11), we find the OPS relation of Eq. (3) should be extended to include TRS,

$$\beta_{ijk}(\omega_\sigma;\omega_1,\omega_2)=\beta_{ijk}(-\omega_\sigma;-\omega_1,-\omega_2) =\beta_{jik}(\omega_1;\omega_\sigma,\omega_2)=\beta_{kji}(\omega_2;\omega_1,\omega_\sigma) . \tag{12}$$

Now by use of OPS and the Hermitian property of the dipole operator $\mathbf{x}$, 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) [4]. In the sum-frequency generation, for example,

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

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 nondisspative optical medium.

OPS alone was examined experimentally in a potassium dihydrogen phosphate (KDP) crystal by looking at an electro-optic (EO) effect and an optical rectification process [9]. It is found that the same parameter governs two different processes of the EO effect and the optical rectification process. Now the extended symmetry relation Eq. (12) predicts that there exists a new relation between two different nonlinear optical processes when degenerate photons are involved. Interestingly, we find that

$$\beta_{ijk}(\omega_\sigma=-2\omega;\omega,\omega)=\beta_{jik}(\omega;\omega_\sigma=-2\omega,\omega)$$
$$=\beta_{jik}(-\omega;-\omega_\sigma=2\omega,-\omega)\ . \qquad (14)$$

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 nondissipative regime of an inorganic crystal such as a KDP crystal. Additionally, the relation Eq. (14) reduces the number of independent nonlinear optical susceptibility tensor components, allowing an efficient design of phase-matching nonlinear optical crystals, for example. The extended symmetry relation, similar to Eq. (12), 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 hyperpolarizabilites $\gamma^{(n)}_{ijk\ldots}(\omega_\sigma;\omega_1,\omega_2,\ldots)$ in a nondissipative optical medium is a consequence of the time-reversal symmetry, as indicated from the time-reversal invariant property of the 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 nondissipative optical medium, rather than two independent symmetries. The relation between the overall permutation and time-reversal symmetry reduces the number of independent nonlinear optical susceptibility tensor components. In a second-order sum-frequency generation process in a nondissipative regime, it is predicted that a second-harmonic generation and a difference-frequency generation are governed by the same parameter.

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