On sum over states (SOS)

Pierre Beaujean

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On the ground of perturbation theory, the SOS expression of Orr and Ward [1] (see also Bishop [2]) states that any component of any nonlinear optical tensor $\chi^{(n)}(-\omega_\sigma; \omega_1, \ldots)$ (of order n)[1] is given by:

$$\chi^{(n)}_{\zeta\eta\ldots\nu}(-\omega_\sigma; \omega_1, \ldots) = \hbar^{-n} \sum_{\mathcal{P}} \sum_{a_1, a_2 \ldots a_n} \frac{\mu^{\zeta}_{0a_1} \mu^{\eta}_{a_1 a_2} \cdots \mu^{\nu}_{a_n 0}}{\prod_{0 < i \leq n}(\omega_{a_i} - \omega_\sigma + \sum_{0 < j < i} \omega_j)}, \tag{1}$$

where $\zeta, \eta, \ldots$ are the Cartesian coordinates x, y, z (in the molecular frame), $\omega_1, \omega_2 \ldots$, the (optical) input frequencies of the laser for the NLO process (with $\omega_\sigma = \sum_{0 < i < n} \omega_i$), $|a_1\rangle, |a_2\rangle, \ldots$, the states of the system **including the ground state** (with $\hbar\omega_{a_i}$ the excitation energy from ground state, noted $|0\rangle$, to $|a_i\rangle$), $\mu^{\zeta}_{a_i a_j} = \langle a_i | \hat{\zeta} | a_j \rangle$ the transition dipole moment from state a_i to a_j (it corresponds to the dipole moment of electronic state a_i when $i = j$), and $\sum_{\mathcal{P}}$ the sum of the different permutations over each pair $(\zeta, \omega_\sigma), (\eta, \omega_1), \ldots$. Given the form of Eq. (1), it is relatively easy to write a (Python) code that compute any $\chi^{(n)}$.

1 Avoiding secular divergence: using fluctuation dipole

Examining the expressions for $n \in [1, 3]$ more closely, one has:

$$\alpha_{ij}(-\omega; \omega) = \hbar^{-1} \sum_{\mathcal{P}} \sum_{a_1} \frac{(\zeta\eta)_{a_1}}{\omega_{a_1} - \omega}, \tag{2}$$

$$\beta_{ijk}(-\omega_\sigma; \omega_1, \omega_2) = \hbar^{-2} \sum_{\mathcal{P}} \sum_{a_1, a_2} \frac{(\zeta\eta\kappa)_{a_1 a_2}}{(\omega_{a_1} - \omega_\sigma)(\omega_{a_2} - \omega_\sigma + \omega_1)}, \tag{3}$$

$$\gamma_{ijkl}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} \sum_{\mathcal{P}} \sum_{a_1, a_2, a_3} \frac{(\zeta\eta\kappa\lambda)_{a_1 a_2 a_3}}{(\omega_{a_1} - \omega_\sigma)(\omega_{a_2} - \omega_\sigma + \omega_1)(\omega_{a_3} - \omega_\sigma + \omega_1 + \omega_2)}, \tag{4}$$

representing the polarizability $\alpha = \chi^{(1)}$, first hyperpolarizability $\beta = \chi^{(2)}$, and second hyperpolarizability $\gamma = \chi^{(3)}$. Here, the numerator notation of Bishop [2], $(\zeta\eta\kappa\lambda)_{a_1 a_2 a_3} = \mu^{\zeta}_{0a_1} \mu^{\eta}_{a_1 a_2} \mu^{\kappa}_{a_2 a_3} \mu^{\lambda}_{a_3 0}$, is employed.

Each of Eqs. (2)-(4) encounters divergences (or singularities) when a denominator vanishes. This phenomenon is termed **secular divergence** if caused by any state $|a_i\rangle = |0\rangle$ (and thus

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[1]I'm aware that χ is generaly used to refer to the nonlinear susceptibility, the macroscopic equivalent of what I'm discussing here, but I needed a greek letter.

$\omega_{a_i} = 0$) or, if any optical frequency (or a combination thereof) matches $\omega_{a_i} \neq 0$, is generally termed **resonance** [2]. While resonances are intrinsic to perturbation theory and often mitigated by introducing damping factors (though methods remain debated [3]), secular divergences are mathematical artifacts and can be avoided.

Following Bishops, substituting the dipole operator in Eq. (1) with a fluctuation dipole operator, $\bar{\mu}_{a_1 a_2}^\zeta = \mu_{a_1 a_2}^\zeta - \delta_{a_1 a_2} \mu_{00}^\zeta$, results in $(\bar{\zeta})_g = 0$, allowing the ground state to be excluded from the summations in Eqs. (2) and (3). Consequently, we obtain:

$$\alpha_{ij}(-\omega;\omega) = \hbar^{-1} \sum_{\mathcal{P}} \sum_{a_1'} \frac{(\zeta\eta)_{a_1}}{\omega_{a_1} - \omega}, \tag{5}$$

$$\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) = \hbar^{-2} \sum_{\mathcal{P}} \sum_{a_1',a_2'} \frac{(\zeta\bar{\eta}\kappa)_{a_1 a_2}}{(\omega_{a_1} - \omega_\sigma)(\omega_{a_2} - \omega_\sigma + \omega_1)}, \tag{6}$$

where the prime indicates that the sums over a_1 (and a_2) now exclude $|0\rangle$. This adjustment removes secular divergence, but also permits the first and last transition dipoles in each term to omit the "bar" as well.

Applying this procedure to Eq. (4) introduces an error in cases where terms with $|a_2\rangle = |0\rangle$ are omitted. The correct expression for the second hyperpolarizability, γ, is therefore the sum of two components, $\gamma = \gamma^{(+)} + \gamma^{(-)}$, where:

$$\gamma_{ijkl}^{(+)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-3} \sum_{\mathcal{P}} \sum_{a_1',a_2',a_3'} \frac{(\zeta\bar{\eta}\bar{\kappa}\lambda)_{a_1 a_2 a_3}}{(\omega_{a_1} - \omega_\sigma)(\omega_{a_2} - \omega_\sigma + \omega_1)(\omega_{a_3} - \omega_\sigma + \omega_1 + \omega_2)},$$

$$\gamma_{ijkl}^{(-)}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-3} \sum_{\mathcal{P}} \sum_{a_1',a_3'} \frac{(\zeta\eta)_{a_1}(\kappa\lambda)_{a_3}}{(\omega_{a_1} - \omega_\sigma)(-\omega_\sigma + \omega_1)(\omega_{a_3} - \omega_\sigma + \omega_1 + \omega_2)}, \tag{7}$$

where $\gamma^{(+)}$ corresponds to the expression when summing over all non-ground states, while $\gamma^{(-)}$ is a correction term, obtained by setting $|a_2\rangle = |0\rangle$ in the expression of $\gamma^{(+)}$. However, these (so-called) secular terms, grouped in $\gamma^{(-)}$, lead to divergence if the conditions $-\omega_\sigma + \omega_1 = \omega_2 + \omega_3 = 0$ is satisfied, even though the ground state is excluded from the summation.

Before addressing this correction in detail, note that a generalization of this procedure yields

$$\chi_{\zeta\eta...\nu}^{(n)}(-\omega_\sigma;\omega_1,\dots) = \chi_{\zeta\eta...\nu}^{(n',+)}(-\omega_\sigma;\omega_1,\dots) + \chi_{\zeta\eta...\nu}^{(n',-)}(-\omega_\sigma;\omega_1,\dots), \tag{8}$$

where $\chi^{(n',+)}$ represents the non-secular contributions, given by:

$$\chi_{\zeta\eta...\nu}^{(n',+)}(-\omega_\sigma;\omega_1,\dots) = \hbar^{-n} \sum_{\mathcal{P}} \sum_{a_1',a_2',\dots} \frac{(\zeta\bar{\eta}\bar{\kappa}\dots\nu)_{a_1 a_2...a_n}}{\prod_{0<i\leq n} \omega_{a_i}'}, \tag{9}$$

which follows directly from Eq. (1), with the summation now excluding the ground state. Here, the notation $\omega_{a_i}' = \omega_{a_i} - \omega_\sigma + \sum_{0<j<i} \omega_j$ is introduced, which will be useful next. The secular

contributions, $\chi^{(n',-)}$, are given by:

$$\chi^{(n',-)} = \sum_{1<i<n} \left[\chi^{(n',+)}\Big|_{|a_i\rangle=|0\rangle} + \sum_{i+1<j<n} \left(\chi^{(n',+)}\Big|_{|a_i\rangle=|a_j\rangle=|0\rangle} + \cdots \right) \right], \qquad (10)$$

where Cartesian indices and laser frequencies have been omitted for clarity. The notation $|a_i\rangle = |a_j\rangle = |0\rangle$ specifies that both states $|a_i\rangle$ and $|a_j\rangle$ are evaluated as the ground state in Eq. (9). The number of secular terms increases with n, as higher-order interactions introduce additional configurations in which intermediate states are the ground state.

After theses formula have been implemented, comparisons between Eq. (1) and Eq. (8) have been successfully conducted to get tensors, $\chi^{(n)}$ corresponding to n^{th}-harmonic generation process (where all $\omega_i = \omega$), up to $n = 6$ (which includes a secular term where $|a_2\rangle = |a_4\rangle = |0\rangle$), within both two- and three-state models.

References

[1] B.J. Orr and J.F. Ward. Perturbation theory of the non-linear optical polarization of an isolated system. *Mol. Phys.*, 20:513–526, 1971.

[2] David M. Bishop. Explicit nondivergent formulas for atomic and molecular dynamic hyper-polarizabilities. *The Journal of Chemical Physics*, 100(9):6535–6542, May 1994.

[3] Jochen Campo, Wim Wenseleers, Joel M. Hales, Nikolay S. Makarov, and Joseph W. Perry. Practical Model for First Hyperpolarizability Dispersion Accounting for Both Homogeneous and Inhomogeneous Broadening Effects. *The Journal of Physical Chemistry Letters*, 3(16):2248–2252, August 2012.