On sum over states (SOS)

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October 31, 2024

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:

$$\chi^{(n)}_{\zeta\eta\ldots\nu}(-\omega_\sigma;\omega_1,\ldots) = \hbar^{-n+1}\sum_{\mathcal{P}}\sum_{a_1,a_2\ldots a_{n-1}} \frac{\mu^{\zeta}_{0a_1}\mu^{\eta}_{a_1a_2}\cdots\mu^{\nu}_{a_{n-1}0}}{\prod_{0<i<n}(\omega_{a_i}-\omega_\sigma+\sum_{0<j<i}\omega_j)}, \tag{1}$$

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 $|a_i\rangle$), $\mu^{\zeta}_{a_ia_j}=\langle a_i|\hat{\zeta}|a_j\rangle$ 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 divergences

Examining the expressions more closely, one has:

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

$$\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) = \hbar^{-2}\sum_{\mathcal{P}}\sum_{a_1,a_2}\frac{(\zeta\eta\kappa)_{a_1a_2}}{(\omega_{a_1}-\omega_\sigma)(\omega_{a_2}-\omega_\sigma+\omega_1)}, \tag{3}$$

$$\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-3}\sum_{\mathcal{P}}\sum_{a_1,a_2,a_3}\frac{(\zeta\eta\kappa\lambda)_{a_1a_2a_3}}{(\omega_{a_1}-\omega_\sigma)(\omega_{a_2}-\omega_\sigma+\omega_1)(\omega_{a_3}-\omega_\sigma+\omega_1+\omega_2)}, \tag{4}$$

representing the polarizability $\alpha=\chi^{(1)}$, first hyperpolarizability $\beta=\chi^{(2)}$, and second hyperpolarizability $\gamma=\chi^{(3)}$. Here, the numerator notation of Bishop [2], $(\zeta\eta\kappa\lambda)_{a_1a_2a_3}=\mu^{\zeta}_{0a_1}\mu^{\eta}_{a_1a_2}\mu^{\kappa}_{a_2a_3}\mu^{\lambda}_{a_30}$, is employed.

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

[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.

$\omega_{a_i} = 0$), can also arise if any optical frequency (or a combination thereof) matches $\omega_{a_i} \neq 0$, generally termed a **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, $\bar{\mu}^{\zeta}_{a_1 a_2} = \mu^{\zeta}_{a_1 a_2} - \delta_{a_1 a_2}\, \mu^{\zeta}_{00}$, 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, permitting 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:

$$\begin{aligned}
\gamma^{(+)}_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) &= \hbar^{-3} \sum_{\mathcal{P}} \sum_{a_1,a_2,a_3}{}' \frac{(\zeta\bar{\eta}\bar{\kappa}\lambda)_{a_1 a_2 a_3}}{(\omega_{a_1} - \omega_\sigma)(\omega_{a_2} - \omega_\sigma + \omega_1)(\omega_{a_3} - \omega_\sigma + \omega_1 + \omega_2)}, \\
\gamma^{(-)}_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) &= \hbar^{-3} \sum_{\mathcal{P}} \sum_{a_1,a_3}{}' \frac{(\zeta\eta)_{a_1}(\kappa\lambda)_{a_3}}{(\omega_{a_1} - \omega_\sigma)(-\omega_\sigma + \omega_1)(\omega_{a_3} - \omega_\sigma + \omega_1 + \omega_2)},
\end{aligned} \tag{7}$$

where $\gamma^{(+)}$ corresponds to the expression when summing over all non-ground states, while $\gamma^{(-)}$ is a correction term, handling $|a_2\rangle = |0\rangle$. However, this (so-called) secular term $\gamma^{(-)}$ leads 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.

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 hyperpolarizabilities. *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.