On sum over states (SOS)

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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:

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

where $i,j,k\ldots$ 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 $\omega_\sigma=\sum_{0<i<n}\omega_i$), $\left|a_1\right\rangle,\left|a_2\right\rangle,\ldots$, the electronic states of the system **including the ground state** (with $\hbar\omega_{a_i}$ the excitation energy from ground state, noted $|0\rangle$, to $|a_i\rangle$), $\mu^r_{a_ia_j}=\langle a_i|\hat{r}|a_j\rangle$ 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 $(i,\omega_\sigma),(j,\omega_1),\ldots$.

In particular, one has:

$$\begin{aligned}
\alpha_{ij}(-\omega;\omega) &= \hbar^{-1}\sum_{\mathcal{P}}\sum_{a_1}\frac{(ij)_{a_1}}{\omega_{a_1}-\omega},\\
\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) &= \hbar^{-2}\sum_{\mathcal{P}}\sum_{a_1,a_2}\frac{(ijk)_{a_1a_2}}{(\omega_{a_1}-\omega_\sigma)(\omega_{a_2}-\omega_\sigma+\omega_1)},\\
\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) &= \hbar^{-3}\sum_{\mathcal{P}}\sum_{a_1,a_2,a_3}\frac{(ijkl)_{a_1a_2a_3}}{(\omega_{a_1}-\omega_\sigma)(\omega_{a_2}-\omega_\sigma+\omega_1)(\omega_{a_2}-\omega_\sigma+\omega_1+\omega_2)},
\end{aligned}$$

with the expression for the polarizability $\alpha=\chi^{(1)}$, the first hyperpolarizability, $\beta=\chi^{(2)}$, and the second hyperpolarizability, $\gamma=\chi^{(3)}$, and where the notation of Bishop [2] for the numerator $(ijkl)_{a_1a_2a_3}=\mu^i_{0a_1}\mu^j_{a_1a_2}\mu^k_{a_2a_3}\mu^l_{a_3\,0}$ is used. Any of these expression leads to divergences (singularities) when the denominator is zero. This is referred to as **secular divergence** if this is due to the fact that any $|a_i\rangle=|0\rangle$ (and thus $\omega_{a_i}=0$), but it can also happen if any of the optical frequencies (or a combination of them) matches $\omega_{a_i}\neq 0$, which one generally refers to as **resonance** [2]. While the latter are inherent to perturbation theory and can be "cured" by introducing damping factors (although the correct way to do so is still debated [3]), the former are purely mathematical, since they can actually be avoided.

[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.

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.