Derivation of the two-level formula for hyperpolarizability

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The sum-of-states (SOS) is a rigorous formalism to calculate (hyper)polarizabilities. The two-level formula for hyperpolarizability can be derived by simplifying the SOS formula in limiting cases.

The full form of SOS formula of component *ABC* of hyperpolarizability is

$$\beta_{ABC}(-\omega_\sigma;\omega_1,\omega_2) = \hat{P}[A(-\omega_\sigma),B(\omega_1),C(\omega_2)]\sum_{i\neq 0}\sum_{j\neq 0}\frac{\mu_{0i}^{A}\overline{\mu_{ij}^{B}}\mu_{j0}^{C}}{(\Delta_i-\omega_\sigma)(\Delta_j-\omega_2)}$$

where

$$\mu_{ij}^{A} = \langle i|\hat{\mu}^{A}|j\rangle \qquad \overline{\mu_{ij}^{A}} = \mu_{ij}^{A} - \mu_{00}^{A}\delta_{ij} \qquad \omega_\sigma = \sum_i \omega_i$$

A,*B*,*C*... denote one of directions {x,y,z}; ω is energy of external fields, and ω=0 corresponds to static electric field; Δ_i stands for excitation energy of state *i* with respect to ground state (0). $\hat{P}$ is permutation operator, for β there are 3!=6 permutations. μ_{ij}^{A} is *A* component of transition dipole moment between state *i* and *j*; when *i*=*j* the term simply corresponds to electric dipole moment of state *i*. $\hat{\mu}$ is dipole moment operator of electron, e.g. $\hat{\mu}^{x} \equiv -x$.

Assume that the charge transfer during electronic excitation is nearly unidirectional (e.g. in direction *Z*), one can safely ignore other components. For component ZZZ of β in static limit, all the six permutations of SOS formula are equivalent, therefore

$$\beta_{ZZZ}^{\mathrm{SOS}} = 6\sum_{i\neq 0}\sum_{j\neq 0}\frac{\mu_{0i}^{Z}\overline{\mu_{ij}^{Z}}\mu_{j0}^{Z}}{\Delta_i\Delta_j}$$

If only one of excited states are taken into account, namely state *i*, then

$$\beta_{ZZZ}^{\mathrm{SOS}} = 6\frac{\mu_{0i}^{Z}\overline{\mu_{ii}^{Z}}\mu_{i0}^{Z}}{\Delta_i^2} = 6\frac{\overline{\mu_{ii}^{Z}}(\mu_{0i}^{Z})^2}{\Delta_i^2}$$

in present case $\overline{\mu_{ii}^{Z}} = \mu_{ii}^{Z} - \mu_{00}^{Z}$, which is variation of dipole moment of excited state *i* and ground state and will be referred to as $\Delta\mu_i^{Z}$.

The oscillator strength between states *i* and *j* is defined as

$$f_{ij} = \frac{2}{3}(E_i - E_j)|\langle i|\boldsymbol{\mu}|j\rangle|^2$$

When only Z component of transition dipole moment is prominent and one of the two states is ground state, the oscillator strength can be written as

$$f_i^Z = \frac{2}{3}\Delta_i(\mu_{0i}^Z)^2$$

The SOS formula now becomes

$$\beta_{ZZZ}^{\mathrm{SOS}} = 6\frac{\Delta\mu_i^Z(\mu_{0i}^Z)^2}{\Delta_i^2} = 6\times(3/2)\frac{\Delta\mu_i^Z f_i^Z}{\Delta_i^3} = 9\frac{\Delta\mu_i^Z f_i^Z}{\Delta_i^3}$$

The $\frac{\Delta\mu_i^Z f_i^Z}{\Delta_i^3}$ term just corresponds the two-level formula frequently involved in literatures.