The "Optical" of Nonlinear Optical Properties

Benoît Champagne

Laboratory of Theoretical Chemistry, Unit of Theoretical and Structural Physical Chemistry, University of Namur, Namur, Belgium

benoit.champagne@unamur.be

Molecular hyperpolarizabilities, the nonlinear responses of the dipole moment to electromagnetic fields, strongly depend on the frequency of the excitation light source. Understanding this frequency dispersion is a prerequisite for interpreting experimental data as well as for designing efficient compounds for NLO applications. Looking back at more than 35 years of predictions of NLO properties by *ab initio* methods, it is obvious that these quantities are difficult to evaluate precisely and that, beyond mean-field approaches, frequency dispersion has often been neglected. To alleviate this issue, it was proposed to combine static hyperpolarizabilities calculated at a highly-correlated level with frequency dispersion estimated at a lower one, typically by using the time-dependent Hartree-Fock method. Sekino and Bartlett [1] proposed a multiplicative scheme whereas an alternative, additive, scheme was put forward by Rice and Handy [2]:

$$\beta_{correlated}(-\omega_\sigma;\omega_A,\omega_B) \approx \beta_{correlated}(0;0,0)\frac{\beta_{TDHF}(-\omega_\sigma;\omega_A,\omega_B)}{\beta_{CPHF}(0;0,0)}$$

$$\beta_{correlated}(-\omega_\sigma;\omega_A,\omega_B) \approx \beta_{correlated}(0;0,0)+\left\{\beta_{TDHF}(-\omega_\sigma;\omega_A,\omega_B)-\beta_{CPHF}(0;0,0)\right\}$$

Since then, many investigations have adopted one or both schemes. Still, not that many studies have addressed their performance. It is now time to see how these two equations have sustained the last 25 years and to review their reliability on selected case studies. Therefore, this poster describes the frequency dispersion of selected molecules (small molecules like CCl_4 as well as NLOphores like *p*-nitroaniline) and it assesses the performance of the two above approximate schemes as well as of other models [3-4]. It also investigates the validity of Kleinmann's symmetry conditions [5].

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