

Time-dependent density functional theory for frequency-dependent nonlinear optical response

Optical materials with enhanced nonlinear optical (NLO) responses have important technological implications¹ such as optical switching and wave-guiding, compact 3D data storage and micro fabrication, chemical and biological sensing, optical power limiting, up-conversion lasing, bio-imaging, etc (e.g. Figure 1). Even though perfecting of synthetic techniques and a growing role of quantum mechanical guidance have led to materials with exceptional hyperpolarizabilities, further progress is still hindered by the cost of both synthetic and characterization methods.

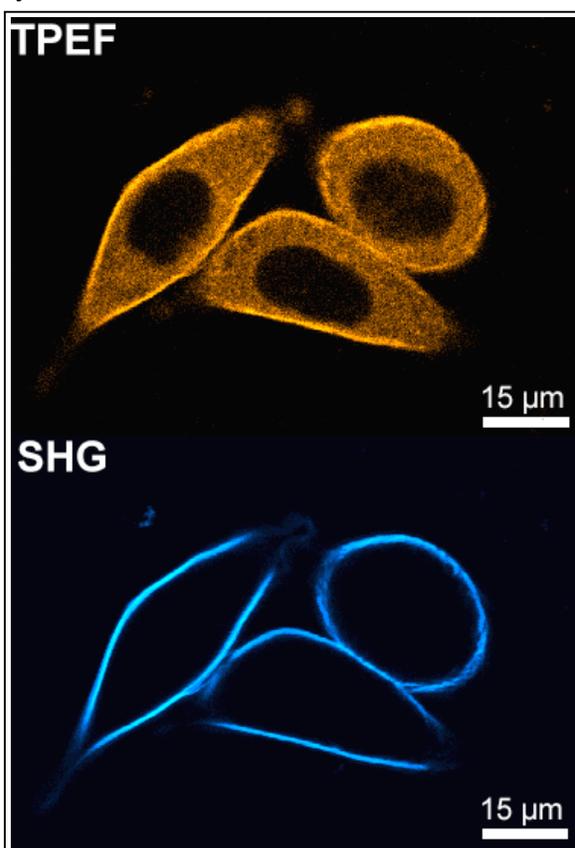


Figure 1. Application example: non-invasive bio-imaging by simultaneous two-photon excited fluorescence and second harmonic generation of isolated Ncad1 cells labeled with an amphiphilic push-pull polyenic chromophore².

Computational design of nonlinear optical materials is a fundamentally difficult problem. Careful and comprehensive analysis is necessary for understanding the key electronic phenomena contributing to NLO properties and their related connections with chemical composition. This is a cornerstone for the

rational design of new NLO materials. First-principles calculations of molecular electronic spectra require extensive numerical effort and, therefore, exact treatment becomes impractical even for fairly small molecules. Correct description of excited states involved in NLO responses frequently requires inclusion of the higher order electronic correlations. This makes their computing a much more complicated procedure compared to analogous ground state calculations. Adiabatic time-dependent density functional theory (TD-DFT) in the Kohn-Sham form has rapidly emerged as an accurate and efficient method for studying the optical response of molecules³. Excellent results have been obtained for organic molecules, organometallic compounds, inorganic finite clusters and infinite crystals.

Recently we have studied the response of the density matrix to an external field in the adiabatic TDDFT theory by mapping the equation of motion for the driven single-electron density matrix into the dynamics of coupled harmonic oscillators. The resulting nonlinear response functions and the closed expressions for arbitrary second and third order frequency-dependent nonlinear polarizabilities have been derived⁴. These expressions include transition densities and frequencies calculated in the linear response TDDFT, and higher order functional derivatives of the exchange-correlation functional. A working code prototype has been developed at Los Alamos as well which computes first, second and third order responses in various regimes using output from the commercial quantum-chemical packages (e.g. Gaussian).

Subsequently, in a benchmark study, we used these equations for computing the third order optical response in the extended molecular systems. TDDFT was applied to calculate one- (linear response) and two- (third-order response) photon absorption spectra in a series of donor-acceptor substituted conjugated molecules. Calculated excitation energies corresponding to one and two-photon absorption maxima are found to be in excellent agreement with experiment for all excitation frequencies across the entire set of molecules (Figure 2)^{5,6}. Usually this is not the case for

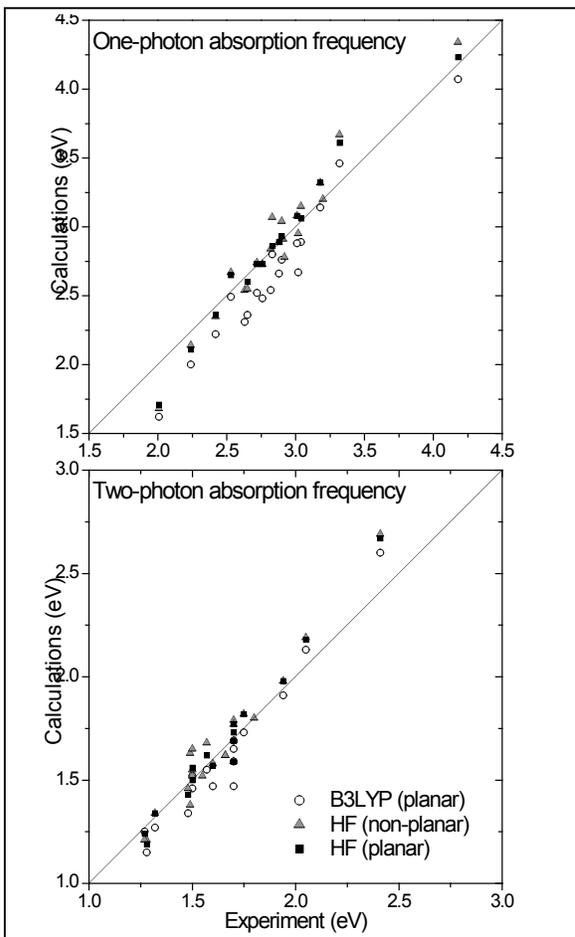


Figure 2. We obtained $\sim 5\%$ (40 nm) average deviation of one-photon and two-photon frequencies of absorption maxima (theory vs. experiment) for series of 20 chromophores (chemical structures are not shown)^{5,6}. For comparison, all calculations reported previously have $>20\%$ (200 nm) errors.

other computational methods. The evaluated two-photon absorption cross-sections agreed with experimental spectroscopy as well.

In a joint experimental-theoretical study of large 3-dimensional substituted organic chromophores (up to 250 atoms in size) we found that the TDDFT gives very good agreement with the experiment predicting correctly complex spectroscopic lineshapes of two-photon absorption related to the third order optical response (Figure 3)⁷. Using the experimental fitting parameters to specify the linewidths dramatically improved the agreement of the theoretical and experimental spectra. The theoretical analysis also led to understanding of the dominant structural factors affecting the linear and nonlinear responses in these large molecular systems featuring strong through-space electronic delocalization^{8,9}.

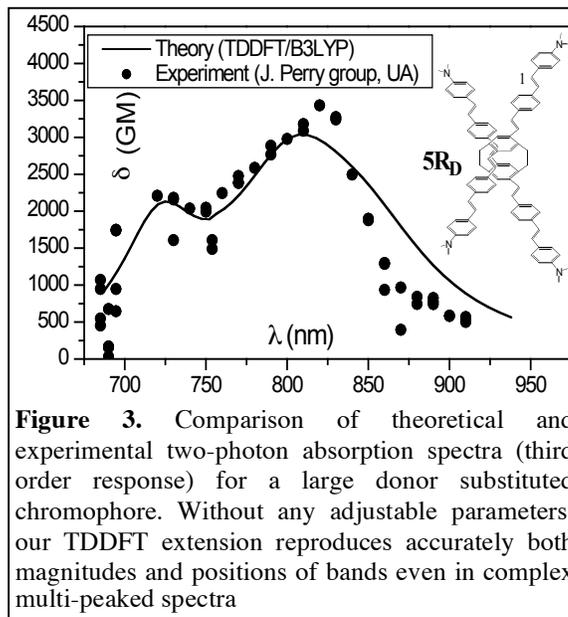


Figure 3. Comparison of theoretical and experimental two-photon absorption spectra (third order response) for a large donor substituted chromophore. Without any adjustable parameters, our TDDFT extension reproduces accurately both magnitudes and positions of bands even in complex multi-peaked spectra

In conclusion, we have developed an efficient formalism for computing frequency-dependent nonlinear optical polarizabilities based on the time-dependent density functional theory⁴⁻⁹. The new approach allows quantitative modeling of NLO responses in complex molecules, enveloping all scales from small molecules to large molecular clusters (200 atoms and more), and to the bulk limit.

References

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