

# NONLINEAR OPTICAL PROPERTIES OF FULLERENES, OLIGOMERS, AND SOLUTIONS

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This work presents development and applications of modern tools in *ab initio* quantum chemistry for obtaining linear and nonlinear response properties of molecules in the gas phase and in solution. The external perturbing fields are primarily electric in nature with frequencies in the optical region.

The framework for this achievement is denoted *response theory*, a formulation of time-dependent perturbation theory, which has been extended to include fourth-order properties fully analytically for self-consistent field (SCF) and multi-configurational SCF (MCSCF) reference states. This extension refers both to the vacuum theory as well as to a self-consistent reaction field model for properties in solution.

Applications are presented, displaying both the possibilities and limitations of the theory. Highly electron correlated MCSCF reference states are used for small molecules both in the gas phase and in solution to obtain accurate values of ground and excited state polarizabilities  $\alpha$ , and ground state hyperpolarizabilities  $\beta$  and  $\gamma$ . Excited state properties are addressed without explicit optimization of the state in question but instead by computing a double residue of the cubic response function. We have in some cases considered both the electronic and the vibrational contributions to these properties. Another direction that has been pursued is to, at the random phase approximation (RPA) level, extend the range of applications for large-scale systems by means of direct atomic orbital driven routines in a parallel scheme. In this context, we address structure-to-property relations for two-dimensional hydrocarbon oligomers, and electron-delocalization of fullerenes. With small we mean molecules with up to 15 atoms and with large-scale we mean molecules with up to 150 atoms.