

Preface

There has been a long-term interest in nonlinear optical (NLO) phenomena, especially as they may be utilized to elucidate physicochemical properties and, more recently, for the development of practical devices in many different fields. A wide variety of processes occurring in either the weak field (perturbative) or strong field (non-perturbative) regime fall under this rubric. Systems that have been investigated range from simple small molecules to large complex bio- and nano-materials and crystalline systems. In either case, advances have been fueled by a combination of experiment and theory. Naturally, the theoretical/computational tools available for larger systems are not as far advanced, but intensive efforts are underway to develop suitable approaches.

One initial approach has been to consider systems that can be modeled as being infinite and periodic. A major computational simplification is then afforded by translational symmetry, although special methods to employ that symmetry are required. On the other hand, structural and chemical deviations from perfect stereoregularity can have important and interesting consequences. It is particularly for such cases that finite-cluster treatments, such as the elongation method (ELG), enter the picture. In general, the finite cluster and infinite periodic approaches have complementary advantages and disadvantages. While exploring the full potentiality of each separately, the possibilities for a symbiotic combination should also be borne in mind.

The elongation method is a very flexible finite cluster approach that has a number of advantageous aspects. It was originally designed to mimic the buildup of an infinite periodic polymer by addition of successive monomer units to a growing chain. However, it is not necessary for the added units to be identical nor is the buildup limited to one-dimensional or quasi-one-dimensional systems. The shape of the system, in fact, is arbitrary. In adding units the elongation method utilizes locality to create a procedure that scales linearly with the size of the system even in cases where partial delocalization must be taken into account. The efficiency depends on the method of localization and, although still evolving, highly satisfactory procedures have already been realized. Moreover, hybrid methods that

include the combination with a partially periodic calculation can readily be foreseen.

This monograph is composed of six chapters. In Chap. 1 we survey the broad range of nonlinear optical properties as well as their various realized and potential applications. This leads to a discussion of nonlinear optical materials. For design purposes one needs to relate the structure of proposed materials to their nonlinear optical (and other) properties, which is a situation where theoretical approaches can be very helpful in providing suggestions for candidate systems that subsequently can be synthesized and studied experimentally. Thus, in Chaps. 2 and 3, we turn to the quantum-mechanical treatment of the response to one or more external oscillating electric fields for molecular (Chap. 2) and macroscopic crystalline (Chap. 3) systems. The systems that can be efficiently studied with the elongation method lie somewhere between these two classes of materials. Thus, the molecular and crystalline systems provide limiting cases whose theoretical treatment can give additional, useful information.

In Chaps. 2 and 3 we present two different ways of including the electric field(s), i.e., by means of the scalar potential or of the vector potential. Whereas our initial focus is on the effective single particle [i.e., Hartree-Fock (HF) or Kohn-Sham density functional theory (KS-DFT)] treatment of the electronic response we include the local MP2 treatment of electron correlation as well. Besides the pure electronic response there is also a nuclear response that gives rise to vibrational NLO properties. The latter can be very important, or even dominant, and cannot be ignored in evaluating the NLO properties. This vibrational contribution can be determined either by perturbation theory or, especially in large systems, by means of the so-called finite (i.e., static) field-nuclear relaxation procedure. In addition, we demonstrate how time/frequency-dependent responses can be calculated using a coupled perturbed theory both at the HF and at the KS-DFT level.

The ELG method is a set of procedures for building up a large system by adding small fragments to an original and growing cluster, one fragment at a time. In Chaps. 4 and 5 we show how this is accomplished by considering, first, the field-free problem at the single particle level. Of particular importance are the procedures for regional molecular orbital localization, as well as integral (and other) cut-offs, that act in concert to allow calculations to be restricted to an interactive region of essentially fixed size which is considerably smaller than the complete system. In carrying out calculations there will sometimes be a limited number of delocalized molecular orbitals that cannot meet the localization criteria. A provision for dealing with this circumstance is described. Building upon the single particle case, we also present our formulation of field-free ELG-LMP2 and ELG-CIS for excited states. Finally, in Chap. 5 we present the adaptations that are utilized in the finite field and, particularly, the coupled perturbation theory treatments (HF; KS-DFT) of NLO properties.

By its very nature the ELG methodology leads to the prediction of linear scaling, which is shown to be verified in practice. Chapters 4 and 5 contain a variety of calculations that establish the efficiency, accuracy, and scope of the ELG approach. The first set of calculations concerns quasilinear systems including conjugated

polymers and chains of water or benzene molecules. Also, ring systems containing porphyrins are discussed. In addition to demonstrating that the computational costs scale linearly with system size, the accuracy of field-free, finite field, and NLO properties is established by comparing with results of conventional molecular calculations. These studies include tests of the ELG treatment of delocalized molecular orbitals. The second set of calculations is presented to demonstrate the applicability of ELG to large systems that are not quasilinear. For such systems there may be significant interactions between fragments that are not directly connected in the buildup process. We show how these interactions can be taken into account within the framework of the ELG method. Moreover, we confirm the efficiency and accuracy achieved for quasilinear systems.

Although the ELG method has advanced considerably since the time of its initial proposal in the early 1990s, there is still much room for improvements and extensions pertinent to NLO as well as other properties. Some specific examples and more general suggestions are given in Chap. 6 together with a concluding summary.



The four authors meeting in Bernie's office in University of California, Santa Barbara, March 15, 2013. From *left to right* Feng Long Gu, Michael Springborg, Yuriko Aoki, Bernard Kirtman

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