Using Patterns to Optimize Nonlinear-Optical Materials

Rick Lytel, Sean Mossman, Ethan Crowell and Mark G. Kuzyk
Department of Physics and Astronomy, Washington State University, Pullman, WA 99164-2814
Email: kuz@wsu.edu

The search for ever-larger nonlinear-optical susceptibilities is fueled by expectations of enabling new devices and technologies. The original theory of the fundamental limits of the nonlinear-optical response for a general quantum system[1] showed that existing systems at that time were far from the limits. This shortfall remains, suggesting that new material design paradigms are required to reach the limit.

The failure to develop better materials lies in our lack of an understanding of the origin of the nonlinear response. Part of the problem is that the nonlinear susceptibilities are not scale invariant properties, so one molecule may be better than another solely based on its electromagnetic size, though its intrinsic response might be weaker. This makes it difficult to pinpoint the critical factors in identifying optimum approaches for designing the ideal quantum systems.

The ratio of the hyperpolarizability β of a system to the upper bound β_{max} defines the scale-invariant intrinsic hyperpolarizability $\beta_{int} = \beta / \beta_{max}$. A comparison of β_{int} of many molecules and quantum systems as a function of parameters that define the system brings a pattern into focus that identifies which parameters are needed to optimize the nonlinear-optical response. A comprehensive search of possible geometries and topologies can identify the promising design patterns for quantum structures.

The result of such a search using quantum wires shows that a short side group placed at a specific point along the wire creates a phase discontinuity of the wave function[2] as shown in the top panel of the figure, leading to a large response. The plot in the middle shows that β_{int} peaks at a particular prong length position. Had β been used rather than β_{int}, the wrong geometry for maximized response would have been identified. Scaling this ideal geometry and topology yields an intrinsic response approaching 0.6, over half the prediction of the original limit theory. Rigorous studies show that 1D "molecules" use electrons more efficiently than a 3D structure,[3] so our work shows that a collection of branched quasi-1D systems are ideal.

The original theory of limits also implied that the nonlinearity could diverge under special circumstances—the many state catastrophe—and that exotic Hamiltonians would be required.[4] Recently, the original theory of limits was replaced by a new theory[5] which properly accounts for the accuracy of sum rules. The new theory predicts a maximum of about 0.7, not unity, consistent with all model studies to date, and nearly achieved by the quantum structure in the top figure.

The new theory shows that the conditions for the many-state catastrophe are unphysical. The bottom plot shows Monte Carlo simulations of the new limit theory compared with the original one. The most significant difference is that a totally new regime for enhanced nonlinearity is found.

The approach of looking for patterns has identified several new paradigms for making quantum systems with large nonlinearity and revealed that conventional molecular design is inconsistent with large intrinsic nonlinearities.

We thank the National Science Foundation (ECCS-1128076) for financial support.

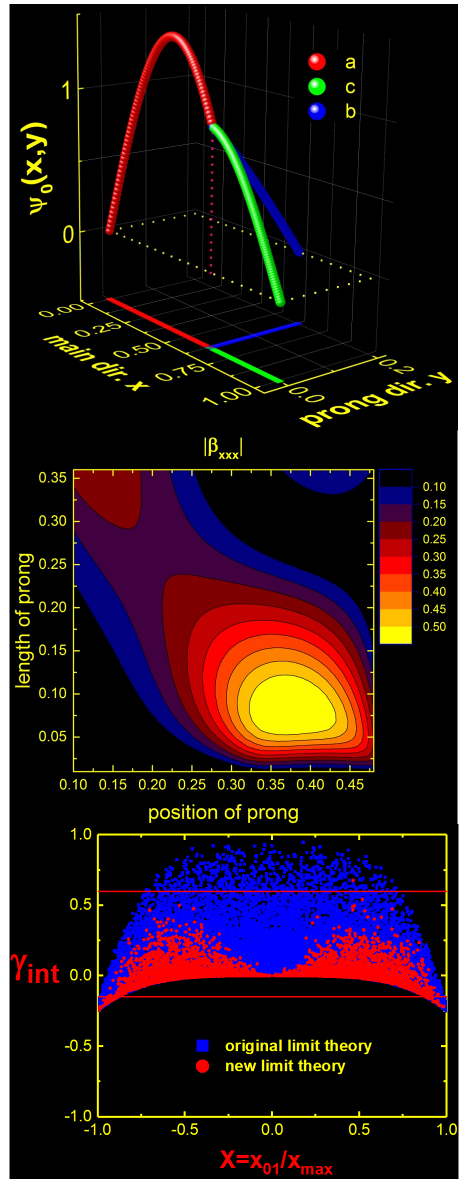

Figure (a) The wave function within a T-shaped quantum graph as shown on the plane below, (b) β_{int} as a function of the prong position and length and (c) scatterplot of the second intrinsic hyperpolarizability as a function of X reveals that the largest response is at X~0.5 rather than X=0, a profound difference between the old and new theories.

[1] M. G. Kuzyk, "Physical Limits on Electronic Nonlinear Molecular Susceptibilities," Phys. Rev. Lett. **85**, 1218 (2000); M. G. Kuzyk, "Fundamental limits on third-order molecular susceptibilities," Opt. Lett. **25**, 1183 (2000).

[2] Rick Lytel, Sean Mossman and Mark G. Kuzyk, "Phase disruption as a new design paradigm for optimizing the nonlinear-optical response," Optics Letters **15**, 4735 (2015).

[3] Mark G. Kuzyk, "A path to Ultralarge Nonlinear-Optical Susceptibilities," J. Opt. Soc. B **33**, E150 (2016).

[4] Shoresh Shafei and Mark G. Kuzyk, "Paradox of the many-state catastrophe of fundamental limits and the three-state conjecture," Phys. Rev. A **88**, 023863 (2013).

[5] Rick Lytel, Sean Mossman, Ethan Crowell and Mark G. Kuzyk, "Exact Fundamental Limits of the First and Second Hyperpolarizabilities," Physical Review Letters **119**, 073902 (2017).