Using Patterns to Optimize Nonlinear-Optical Materials
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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 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 $\beta$ of a system to the upper bound $\beta_{\text{max}}$ defines the scale-invariant intrinsic hyperpolarizability $\beta_{\text{int}} = \beta / \beta_{\text{max}}$. A comparison of $\beta_{\text{int}}$ 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 as shown in the top panel of the figure, leading to a large response. The plot in the middle shows that $\beta_{\text{int}}$ peaks at a particular prong length position. Had $\beta$ been used rather than $\beta_{\text{int}}$, 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, so our work shows that a collection of branched quasi-1D structures are ideal.

The original theory of limits also implied that the nonlinear response could diverge under special circumstances—the many state catastrophe—and that exotic Hamiltonians would be required. Recently, the original theory of limits was replaced by a new theory 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.

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