Maximizing the hyperpolarizability of one-dimensional systems

Urszula B. Szafruga and Mark G. Kuzyk

Department of Physics and Astronomy, Washington State University, Pullman, Washington 99164-2814

David S. Watkins

Department of Mathematics, Washington State University, Pullman, Washington 99164-3113

Abstract

Previous studies have used numerical methods to optimize the hyperpolarizability of a one-dimensional quantum system. These studies were used to suggest properties of one-dimensional organic molecules, such as the degree of modulation of conjugation, that could potentially be adjusted to improve the nonlinear-optical response. However, there were no conditions set on the optimized potential energy function to ensure that the resulting energies were consistent with what is observed in real molecules. Furthermore, the system was placed into a one-dimensional box with infinite walls, forcing the wavefunctions to vanish at the ends of the molecule. In the present work, the walls are separated by a distance much larger than the molecule’s length; and, the variations of the potential energy function are restricted to levels that are more typical of a real molecule. In addition to being a more physically-reasonable model, our present approach better approximates the bound states and approximates the continuum states - which are usually ignored. We find that the same universal properties continue to be important for optimizing the nonlinear-optical response, though the details of the wavefunctions differ from previous result.
I. INTRODUCTION

The nonlinear-optical susceptibility is a material property that describes the strength of light-matter interactions and is the basis for applications such as optical switching, which is used in telecommunications,
three-dimensional nano-photolithography used in making small structures,
and making new materials for novel cancer therapies. Quantum calculations show that there is a limit to the nonlinear-optical response. This limit provides a target for making optimized materials and is useful for defining scaling laws that can be used to determine the intrinsic properties of a molecule. In this work, we focus on the second-order susceptibility and the underlying molecular hyperpolarizability, which is the basis of electro-optic switches and frequency doublers.

We consider linear molecules in a potential well. In previous work, the molecule was situated in an infinite well, and arbitrarily large variations of the potential were allowed. In the current work, in an effort to make our molecules more realistic, we model them with a potential well of a depth not exceeding 8 eV, and we place the walls of the infinite well far from the molecule compared with its electronic size. As described later, under these conditions we were able to obtain intrinsic hyperpolarizabilities of as much as 0.708, which is about as big as we got in the previous studies.

The fundamental limit of the off-resonance hyperpolarizability is given by,

\[ \beta_{MAX} = \frac{4}{\sqrt{3}} \left( \frac{e \hbar}{\sqrt{m}} \right)^3 \frac{N^{3/2}}{E_{10}^{7/2}}, \]  

(1)

where \( N \) is the number of electrons and \( E_{10} \) the energy difference between the first excited state and the ground state, \( E_{10} = E_1 - E_0 \). Using Equation (1), we can define the off-resonant intrinsic hyperpolarizability, \( \beta_{int} \), as the ratio of the actual hyperpolarizability (measured or calculated), \( \beta \), to the fundamental limit,

\[ \beta_{int} = \beta / \beta_{MAX}. \]  

(2)

The intrinsic hyperpolarizability is a scale-invariant quantity because it does no depend on the number of electrons or on scale, as defined in the literature. Thus, it allows one to compare molecules of very different structures and sizes. We note that since the dispersion of the fundamental limit of \( \beta \) is also known, it is possible to calculate the intrinsic hyperpolarizability at any set of wavelengths for any second-order phenomena. In the present work, we treat only the zero-frequency limit.
Prior to 2007, an analysis of a large set of molecules showed that the largest nonlinear susceptibilities of the best ones fell short of the fundamental limit by a factor of about 30[10,17,18], or $\beta_{int} \leq 0.03$. This shortfall was shown to not be of a fundamental nature.[18]

Later, a molecule with asymmetric conjugation of modulation was measured to have $\beta_{int} = 0.048$.[19] suggesting that even larger values might be possible.

In the present work, we apply numerical optimization using methods similar to that of Zhou and coworkers.[12] This work led Zhou and coworkers to propose that modulated conjugation in the bridge between donor and acceptor ends of a molecule may be a new paradigm for making molecules with higher intrinsic hyperpolarizability,[12] a hypothesis that was experimentally investigated by Pérez Moreno.[19] Here, we investigate weather or not the same behavior is observed in our more restricted parameter space.

We also investigate universal scaling, the observation that a broad range of quantum systems whose hyperpolarizability is at the fundamental limit share certain properties.

II. COMPUTATIONAL APPROACH

Each one-dimensional molecule is modeled by a potential function. The potential is fixed at zero in the buffer regions and takes on negative values between 0 and -8 eV in the region that represents the molecule. In that region the potential function is piecewise linear with 39 degrees of freedom. In previous studies we have used cubic splines to represent the potential functions. We switched to piecewise polynomials so that the potential would nowhere inadvertently overshoot the constraints $0 > V(x) > -8 eV$.

Starting from a given potential function, we use the Nelder-Mead simplex algorithm[20] to vary the potential to maximize $\beta_{int}$. Since there are 39 degrees of freedom, we are maximizing over a 39-dimensional space. We have three ways of computing $\beta$, all of which require solving the one-dimensional Schroedinger eigenvalue problem for the given potential (and in some cases also for neighboring potentials). We solve the eigenvalue problem numerically on a computational mesh consisting of 400 quadratic finite elements[21] with a total of 799 degrees of freedom. Half of the elements are devoted to the part of the computational domain that represents the molecule, and the other half cover the buffer regions between the molecule and the infinite walls. The mesh is finest in the region that represents the molecule and becomes coarser as one moves from the molecule toward either wall.
Once we have solved the eigenvalue problem, we can compute transition moments and then obtain $\beta$ by the standard Orr and Ward SOS expression $\beta_{SOS}$, the dipole free expression $\beta_{DF}$, or a finite difference approximation $\beta_{NP}$, which is described in the literature. In the optimization code we use $\beta_{NP}$. That is, we seek to maximize $\beta_{int} = \beta_{NP}/\beta_{MAX}$. Once the optimization is complete, we use $\beta_{SOS}$ and $\beta_{DF}$ for comparison to check the accuracy of the result.

The exact computation of $\beta_{SOS}$ and $\beta_{DF}$ requires sums over infinitely many states. We approximate them by summing over the 80 lowest energy levels. This is overkill; typically 20 or 30 states give a sufficiently accurate approximation. All computations are done using MATLAB.

In addition to calculating the hyperpolarizability using the three equivalent methods, we also compute the matrix $\tau$, which represents deviations from the sum rules and is defined by

$$\tau_{mp}^{(N)} = \delta_{m,p} - \frac{1}{2} \sum_{n=0}^{N} \left( \frac{E_{nm}}{E_{10}} + \frac{E_{np}}{E_{10}} \right) \frac{x_{mn}}{x_{10}^{\text{max}}} \frac{x_{np}}{x_{10}^{\text{max}}} x_{mn} x_{np},$$

(3)

where $x_{10}^{\text{max}}$ is the magnitude of the fundamental limit of the position matrix element $x_{10}$ for a one electron system, and is given by,

$$x_{10}^{\text{max}} = \frac{\hbar}{\sqrt{2mE_{10}}}.$$

(4)

Each matrix element of $\tau^{(N)}$, indexed by $m$ and $p$, is a measure of how well the $(m, p)$ sum rule is obeyed when truncated to $N$ states. If the sum rules are exactly obeyed, $\tau_{mp}^{(\infty)} = 0$ for all $m$ and $p$. We use 80 states ($N = 80$) when calculating the $\tau$ matrix or the hyperpolarizability with an SOS expression so that truncation errors are kept to a minimum. In addition, since the hyperpolarizability depends critically on the transition dipole moment from the ground state to the excited states, we use the value of $\tau_{00}^{(80)}$ as an important test of the accuracy of the calculated wavefunctions.

III. RESULTS AND DISCUSSIONS

Since the Nelder-Mead algorithm only gives a local optimum, we arrive at different optimized potentials from different starting potentials. We tried the same starting potential functions as used by Zhou and coworkers. More precisely, the shapes were the same, but we rescaled them to fit within our new constraints.
FIG. 1: Optimized potential energy function and first 15 wavefunctions after 9450 iterations. Starting potential is $V(x) = 0$.

FIG. 2: Close up view of Figure 1 showing the part of the domain that represents the molecule.

Figure 1 shows an example of the optimized potential energy function after 9,450 iterations when starting with the potential $V(x) = 0$. Figure 2 shows an expanded view of only the potential well of the molecule. Also shown in Figures 1 and 2 are the eigenfunctions of the first 15 states and 8 states, respectively, computed from the optimized potential. First, we note that the potential energy function shows the same kinds of wiggles as in our original paper,[12] though not of sufficient amplitude to localize the wavefunctions.

In previous work,[13] Zhou and coworkers found that the intrinsic hyperpolarizability is
FIG. 3: Optimized potential energy function and first 15 wavefunctions after 4,079 iterations. Starting potential is $V(x) = x$.

FIG. 4: Close up view of Figure 3 showing the part of the domain that represents the molecule. Optimized for two broad classes of potential energy functions. One in which the potential energy function is characterized by wiggles, as is the type shown in Figure 1 and another, in which the potential energy functions are relatively smooth, as shown in Figure 3, an example of the optimized potential energy function when starting with the potential $V(x) = x$. (Also shown are the eigenfunctions of the first 15 states computed with the optimized potential.) However, in contrast to past work, both of these potentials lead to a large degree in overlap between the energy eigenfunctions.
FIG. 5: Close up view of Potential energy and wavefunction when the intrinsic hyperpolarizability is optimized. Starting potential is $x + 10 \sin(x)$.

Figure 5 shows the optimized potential energy function for a starting potential of the form $x + 10 \sin(x)$. The potential energy function is characterized by large oscillations and the wavefunctions are bimodally localized near $x = \pm 0.8$. However, the wavefunctions are not each individually localized in a unique region as was found for the case Studied by Zhou, when the amplitude of wavefunction oscillations was not restricted.

As found in our previous work, the optimized potentials each share certain universal properties.[15] For example, when the intrinsic hyperpolarizability is optimized, only two excited states dominate the sum-over states expression, that is, two excited states are responsible for over 90% of the hyperpolarizability. This is consistent with the three-level ansatz.

Table 1 summarizes the results for the full set of calculations. This table includes the values of the optimized hyperpolarizability for all three methods of calculation, as well as the hyperpolarizability of the starting potential. The SOS and DF values were calculated after
TABLE I: Summary of calculations with different starting potentials. $\beta_s$ is the hyperpolarizability of the starting potential while the other ones are after optimization. The transition moments and energies are in dimensionless units. When one desires $x_{nm}$ to be in units of angstroms, then energies would be determined by multiplying all values of $E_{n0}$ by $\hbar^2/ma^2$, with $a = 10^{-10}$ m (1 Å). In this case, the energy is in units of $1.2 \times 10^{-18}$ J or about 7.6 eV.

| $V(x)$ | $\beta_S$ | $\beta_{SOS}$ | $\beta_{DF}$ | $\beta_{NP}$ | $\tau_{(80)}^{(80)}$ | $E_{10}$ | $E_{20}$ | $x_{00}$ | $x_{10}$ | $x_{20}$ | $x_{11}$ | $x_{21}$ | $x_{22}$ | $\tau_{max}$ | $E_{max}$ |
|--------|-----------|---------------|-------------|-------------|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0      | 0         | 0.6859        | 0.6705      | 0.6859      | 0.0122          | 0.020  | 0.045 | -5.880 | -3.911 | 1.406  | 2.757  | 5.531  | 2.855  | -0.786 | 0.453  |
| $\tanh(x)$ | 0.0507   | 0.7073        | 0.6841      | 0.7071      | 0.011           | 0.100  | 0.208 | -9.660 | 1.760  | -0.602 | -5.663 | -2.561 | -4.414 | 0.789  | 0.484  |
| $x$    | 0.6447    | 0.7081        | 0.6936      | 0.7080      | 0.0069          | 0.119  | 0.247 | -9.562 | -1.619 | 0.551  | -5.894 | 2.347  | -4.682 | -0.789 | 0.482  |
| $x^2$  | 0.5568    | 0.7084        | 0.7054      | 0.7084      | 0.0013          | 0.088  | 0.182 | -8.501 | -1.881 | 0.643  | -4.227 | 2.734  | -2.871 | -0.789 | 0.483  |
| $\sqrt{x}$ | 0.6650    | 0.7071        | 0.6809      | 0.7068      | 0.0127          | 0.114  | 0.237 | -9.812 | -1.656 | 0.574  | -6.060 | 2.402  | -5.045 | -0.789 | 0.479  |
| $x + \sin x$ | 0.4854    | 0.7078        | 0.6973      | 0.7077      | 0.0052          | 0.115  | 0.240 | -9.498 | -1.645 | 0.561  | -5.776 | 2.383  | -4.557 | -0.790 | 0.481  |
| $x + 10 \sin x$ | 0.2248    | 0.6822        | 0.6875      | 0.6821      | 0.0056          | 0.191  | 0.413 | -6.300 | -1.278 | 0.497  | -9.138 | -1.820 | -8.979 | -0.791 | 0.463  |

Optimizing $\beta_{NP}$. $\beta_{NP}$ and $\beta_{SOS}$ agree to within about 0.1%, suggesting that the numerical calculations are accurate. $\beta_{DF}$ is typically within 5% of the other two, which is commonly observed when $\beta_{DF}$ and $\beta_{SOS}$ have converged.\[23, 25\]

Table 1 shows that all optimized intrinsic hyperpolarizabilities, independent of the starting potential, are around 0.7 and never larger than 0.708. Also $E_{10}/E_{20}$ is between 0.45 and 0.49, and $x_{10}/x_{10}^{max} \approx 0.79$ for all optimized potentials. This universal behavior is in agreement with previous 1D\[12–15\] calculations, calculations that optimize the positions of nuclei in 2D,\[26\] and when the effects of externally-applied electromagnetic fields are included.\[27\]

Thus, we find that in the more restrictive case where the amplitude of changes in the potential energy function are constrained, and when moving the walls away from the molecule to approximate continuum states, the universal properties that are observed have not changed. However, while the three-level ansatz continues to be observed, we have not observed full localization of the wavefunctions. But, we do observe the same sort of oscillations, suggesting that modulation of conjugation may yet prove to be a good paradigm for enforcing the three-level ansatz and resulting in an optimized nonlinear-optical response of real molecules.\[28\]
IV. CONCLUSION

Many potential energy functions, even in the more restricted case studied here, are found to bring the intrinsic hyperpolarizability close to the fundamental limit. In particular, there appear to be two classes of potentials that approach this limit. First, the wiggly potential energy functions are found to have only somewhat spatially separated eigenfunctions. These potentials led to the prediction that modulation of conjugation may show promise for higher values of the intrinsic hyperpolarizability. The second class was characterized by much smaller wiggles. Though the shapes of these potentials varied significantly, they were found to have several features in common. In particular, upon optimization, $\beta_{int}$ approached 0.71, $E_{10}/E_{20}$ is between 0.45 and 0.49 and $x_{10}/x_{10}^{\text{max}} \approx 0.79$. Also, when the hyperpolarizability is optimized the system is dominated by three states, so the three-level ansatz holds.

It is interesting that so many differently shaped potentials end up having so many similar characteristics and that they share certain universal properties. This hints at the possibility for new underlying physics. Since there appear to be a large number of different potential energy functions that lead to a maximized intrinsic hyperpolarizability, it may be possible to use this fact to engineer molecules that achieve ever larger intrinsic hyperpolarizabilities that approaches the fundamental.

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