Topological Optimization of Nonlinear Optical Quantum Wire Networks (plus extra content)

Rick Lytel, Shoresh Shafei, and Mark G. Kuzyk

Department of Physics,
Washington State University

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Topics

The quantum graph as an optimized model of a nonlinear optical, quantum-confined system

How to calculate nonlinearities of quantum graphs

Topological dependence of nonlinearities

Scaling properties near maximum response

Implications for molecular and nanoscale systems

Progress of research in NLO quantum graphs

Confinement-enhanced nonlinearities

"Effect of extreme confinement on the nonlinear optical response of quantum wires," S. Shafei and M.G. Kuzyk, J Non Opt Phys Mat 20, 427 (2011).

Quasi-quadratic energy spectra with tunable ground states

"Critical role of the energy spectrum in determining the nonlinear optical response of a quantum system," S. Shafei and M.G. Kuzyk, J Op Soc Am B 28, 882 (2011).

Topological and geometric localization of eigenstates

"Geometry-controlled nonlinear optical response of quantum graphs," S. Shafei, R. Lytel, and M.G. Kuzyk, J. Opt. Sci. Am. B 29, 3419 (2012).

" Influence of geometry and topology of quantum graphs on their nonlinear optical properties," R. Lytel, S. Shafei, J.H. Smith, and M.G. Kuzyk, Phys. Rev. A 87, 043824 (2013).

Scalable to many-electrons and complex molecular-like structures

S. Shafei, R. Lytel, and M.G. Kuzyk, in preparation.

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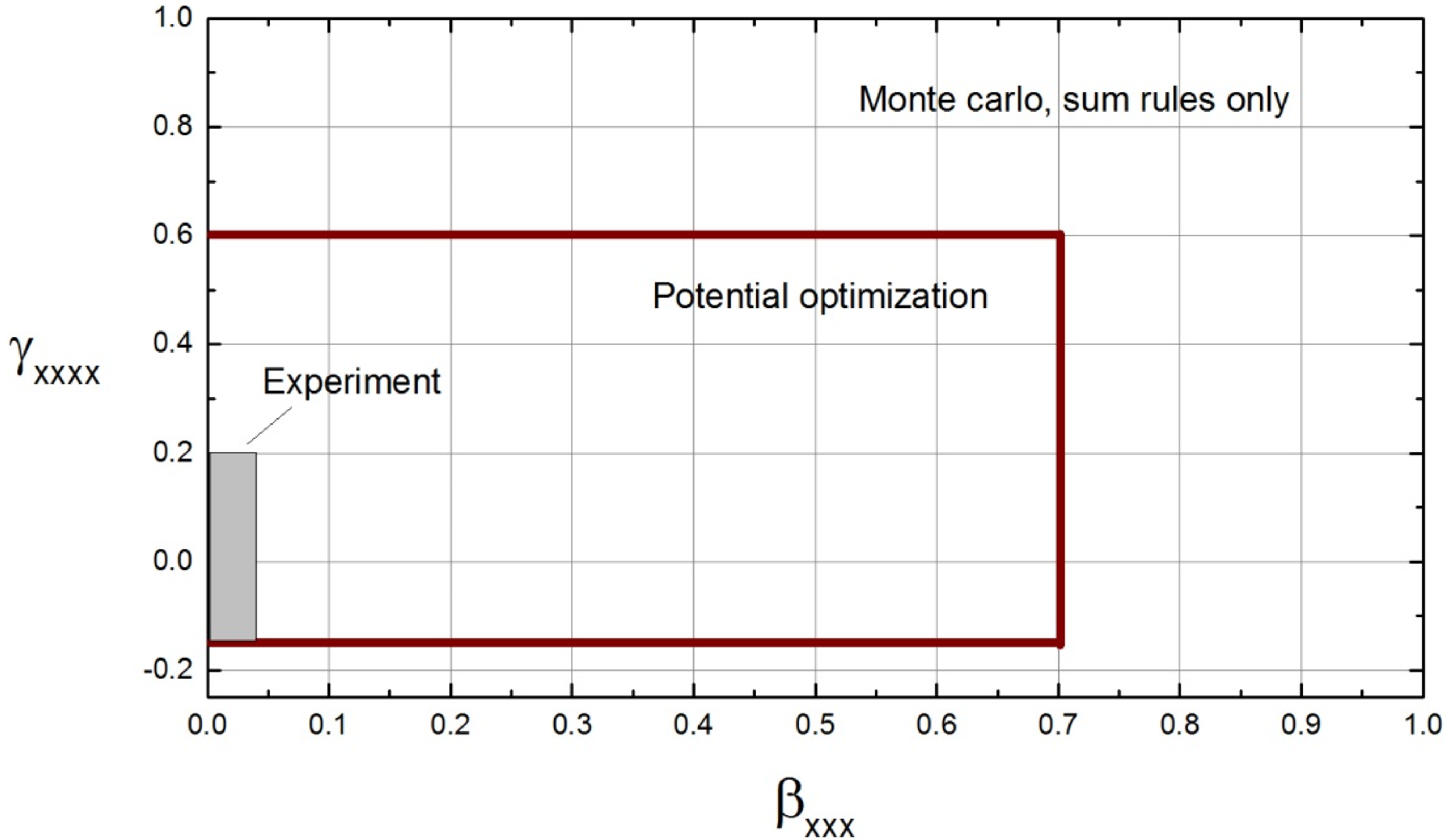
Off-resonance, intrinsic hyperpolarizability limits



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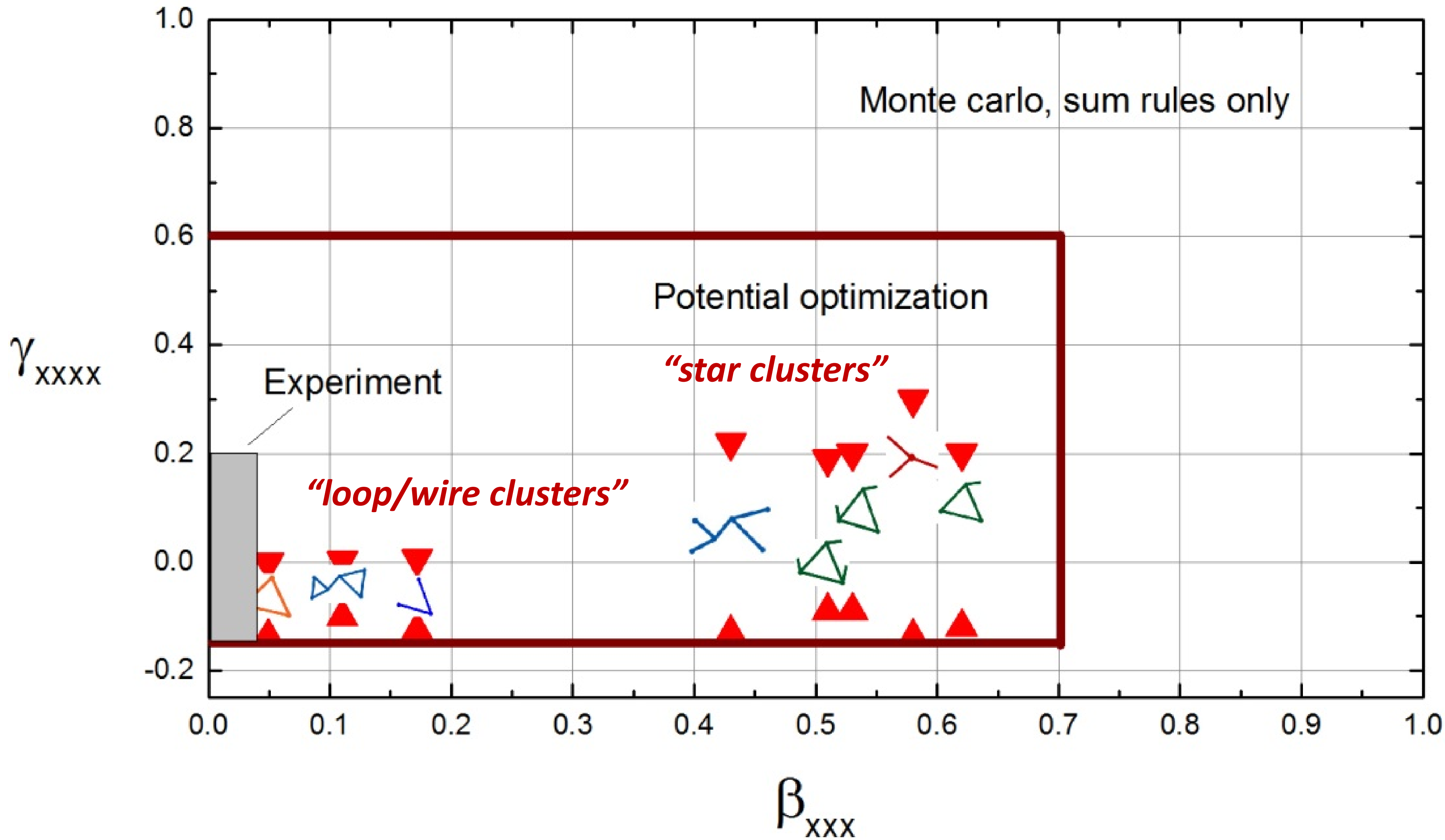
Why quantum graphs are interesting



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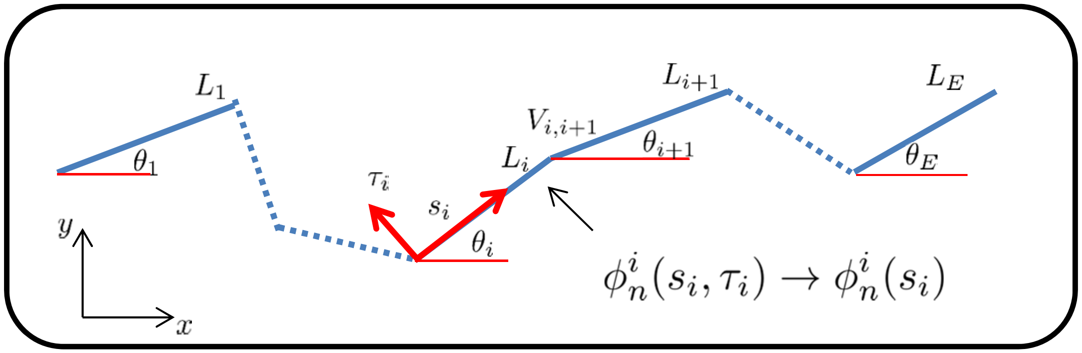
Quantum mechanics of bare graphs



Extreme confinement along τ

Electron dynamics along s

Self-adjoint Hamiltonian

Zero potential everywhere

Eigenfunctions are unions of edge functions having same eigenvalues

$$H\psi_n(s) = E_n\psi_n(s) \qquad \psi_n(s) = \cup_{i=1}^{E}\phi_n^i(s_i) \qquad H\phi_n^i = E_n\phi_n^i$$

Edge functions: continuity and conservation of probability flux

$$\phi_n^i = A_n^{(i)}\sin k_n s_i + B_n^{(i)}\cos k_n s_i \qquad \phi_n^i = \phi_n^{i+1}\ at\ V_{i,i+1}$$

'degree' of vertex

$$\sum_{i=1}^{d}\phi_n'^i = 0\ at\ V_{i,i+1}$$

Homogeneous, coupled linear equations for amplitudes

$$\sum_{i=1}^{2E} a_n^{ij}C_n^{(i)} = 0,\ j = 1,2,3\ldots 2E,\ C_n^{(1)} = A_n^{(1)},\ C_n^{(2)} = B_n^{(1)}\ldots$$

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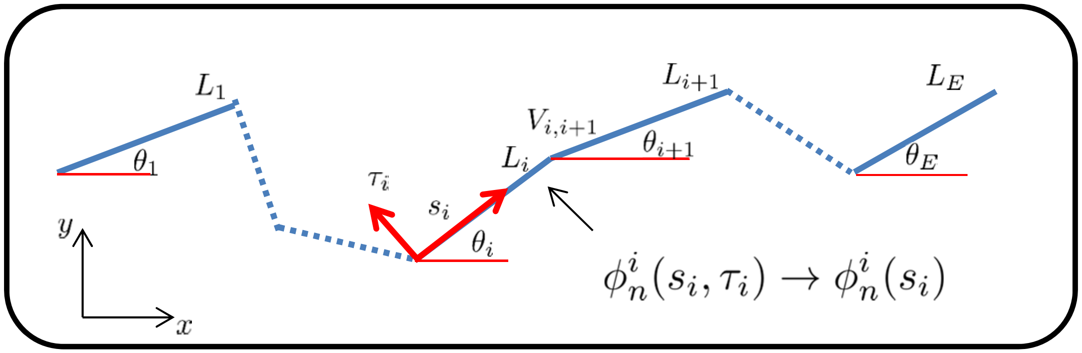
Quantum mechanics of δ-dressed graphs



Extreme confinement along τ

Electron dynamics along s

Self-adjoint Hamiltonian

V= (g/L)δ(s) at a vertex

Eigenfunctions are unions of edge functions having same eigenvalues

$$H\psi_n(s) = E_n\psi_n(s) \qquad \psi_n(s) = \cup_{i=1}^{E}\phi_n^i(s_i) \qquad H\phi_n^i = E_n\phi_n^i$$

Edge functions: continuity and conservation of probability flux

$$\phi_n^i = A_n^{(i)}\sin k_n s_i + B_n^{(i)}\cos k_n s_i \qquad \phi_n^i = \phi_n^{i+1} \ at \ V_{i,i+1}$$

'degree' of vertex

$$\sum_{i=1}^{d}\phi_n^{\prime i} = 2(g/L)\phi_n(a)$$

Homogeneous, coupled linear equations for amplitudes

$$\sum_{i=1}^{2E} a_n^{ij}C_n^{(i)} = 0,\ j = 1,2,3...2E,\ C_n^{(1)} = A_n^{(1)},\ C_n^{(2)} = B_n^{(1)}...$$

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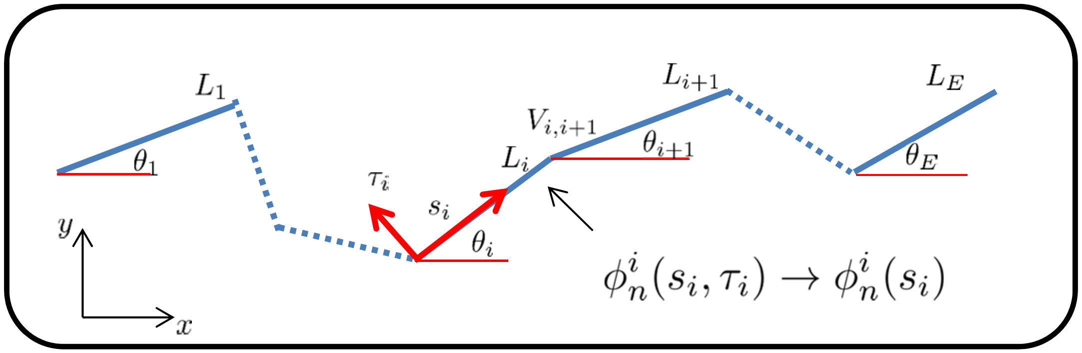
Quantum mechanics of graphs (cont'd)



Extreme confinement along τ

Electron dynamics along s

Self-adjoint Hamiltonian

Bare or dressed edges

Determinant of coefficients vanishes yielding secular equation for eigenvalues

$$\det a_n^{ij} = 0 \qquad f_{sec}(k_n; L_i, \theta_i) = 0 \Rightarrow E_n = k_n^2/2$$

Continuity equations for amplitudes, plus normalization yields amplitudes

$$\phi_n^i = A_n^{(i)} \sin k_n s_i + B_n^{(i)} \cos k_n s_i$$

Transition moments are now calculable

$$r_{nm} = \sum_{i=1}^{E} \int_i ds_i \; r(s_i) \phi_n^{*i}(s_i) \phi_m^i(s_i)$$

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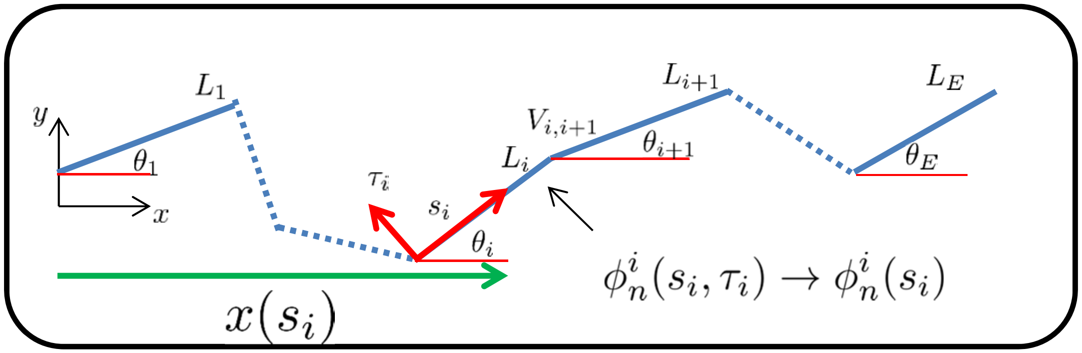
Sum rules for quasi-1D quantum graphs



$$\phi_n^i(s_i) \equiv |\phi^i(s_i))$$

$$x(s_i) = \sum_{l=1}^{i-1} L_l \cos\theta_l + s_i \cos\theta_i$$

$$S_{nm} = \sum_{p=0}^{\infty} \left[2E_{p0} - (E_{n0} + E_{m0})\right] x_{np} x_{pm} = \delta_{nm}$$

$$S_{nm} = S_{nm}^L + S_{nm}^T$$

$$S_{nm}^L = \sum_{p=0}^{\infty} \left(\left[2E_{p0} - (E_{n0} + E_{m0})\right] \sum_{i=1}^{E} (\phi_n^i | x(s_i) | \phi_p^i) \sum_{j=1}^{E} (\phi_p^j | x(s_j) | \phi_m^j) \right)$$

$$S_{nm}^T = \sum_{i=1}^{E} (\phi_n^i | \phi_m^i) \sin^2\theta_i$$

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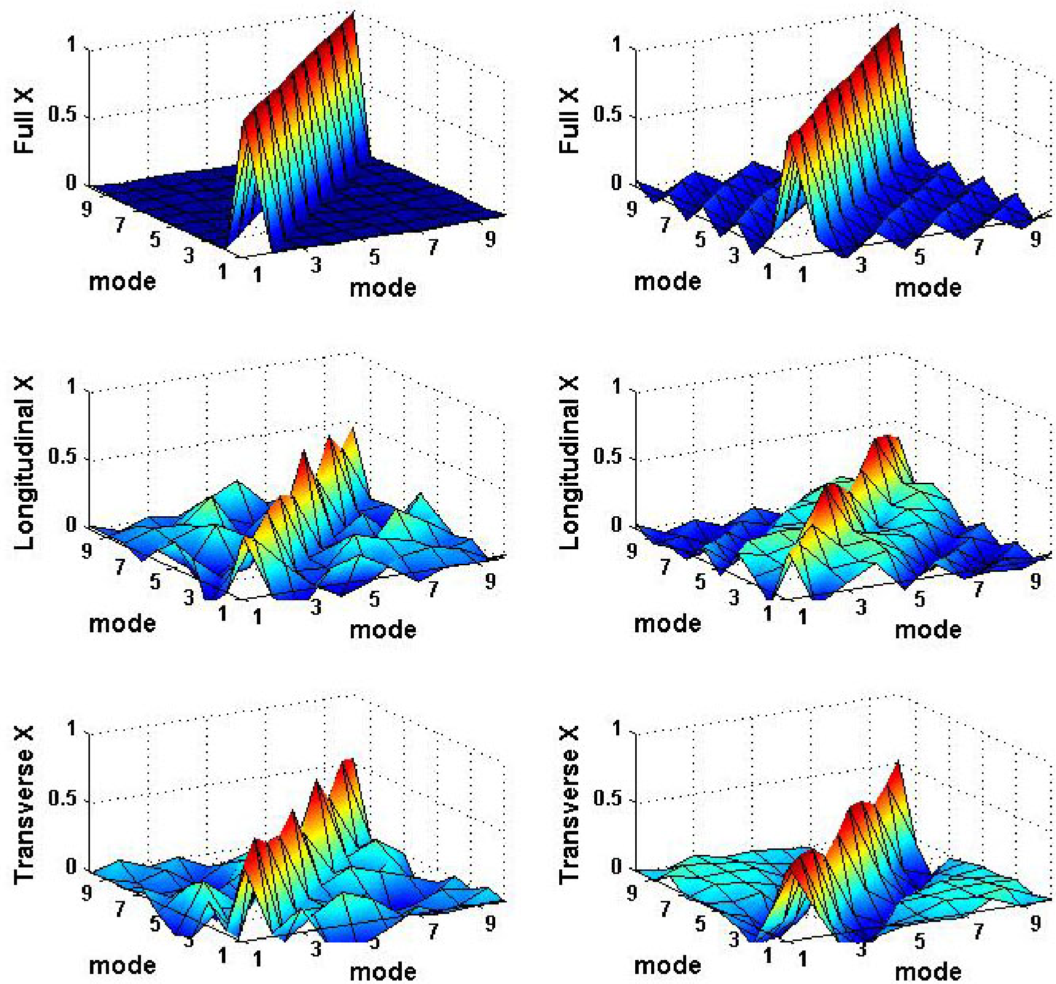
Sum rules: Exquisite accuracy check



Correct eigenstates

Missing eigenstates

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First hyperpolarizability tensor

$$\beta_{ijk} = -\frac{e^3}{2}{\sum_{n,m}}' \frac{1}{E_{n0}E_{m0}}\left(r^i_{0n}\bar{r}^j_{nm}r^k_{m0} + r^i_{0n}\bar{r}^k_{nm}r^j_{m0} + r^k_{0n}\bar{r}^i_{nm}r^j_{m0} + h.c\right)$$

Fully symmetric 3rd rank Cartesian tensor

$$\begin{aligned}\beta_{xxx}(\theta) &= \beta_{xxx}\cos^3\theta + 3\beta_{xxy}\cos^2\theta\sin\theta \\ &+ 3\beta_{xyy}\cos\theta\sin^2\theta + \beta_{yyy}\sin^3\theta\end{aligned}$$

Four independent components relating lab and graph frames

$$|\beta| = \sqrt{\beta_{xxx}^2 + 3\beta_{xxy}^2 + 3\beta_{xyy}^2 + \beta_{yyy}^2}$$

Tensor norm (invariant under rotations of graph)

$$\beta_{max} = 3^{1/4}\left(\frac{e\hbar}{\sqrt{m}}\right)^3\left(\frac{N^{3/2}}{E_{10}^{7/2}}\right) \quad \longrightarrow \quad -1 \leq \beta_{int} \equiv \frac{\beta}{\beta_{max}} \leq 1$$

Normalization for scale-invariant calculations

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Second hyperpolarizability tensor

$$\gamma_{ijkl} = (1/6)P_{ijkl}\left(\sum_{n,m,l}{}' \frac{r^i_{0n}\bar{r}^j_{nm}\bar{r}^k_{ml}r^l_{l0}}{E_{n0}E_{m0}E_{l0}} - \sum_{n,m}{}' \frac{r^i_{0n}r^j_{n0}r^k_{0m}r^l_{m0}}{E^2_{n0}E_{m0}}\right)$$

Fully symmetric 4th rank Cartesian tensor

$$\begin{aligned}\gamma_{xxxx}(\theta) &= \gamma_{xxxx}\cos^4\theta + 4\gamma_{xxxy}\cos^3\theta\sin\theta \\ &+ 6\gamma_{xxyy}\cos^2\theta\sin^2\theta + 4\gamma_{xyyy}\cos\theta\sin^3\theta \\ &+ \gamma_{yyyy}\sin^4\theta\end{aligned}$$

Five independent components relating lab and graph frames

$$|\gamma| = \sqrt{\gamma^2_{xxxx} + 4\gamma^2_{xxxy} + 6\gamma^2_{xxyy} + 4\gamma_{xyyy} + \gamma^2_{yyyy}}$$

Tensor norm (invariant under rotations of graph)

$$\gamma_{max} = 4\left(\frac{e^4\hbar^4}{m^2}\right)\left(\frac{N^2}{E^5_{10}}\right) \longrightarrow -1/4 \leq \gamma_{int} \equiv \frac{\gamma}{\gamma_{max}} \leq 1$$

Normalization for scale-invariant calculations

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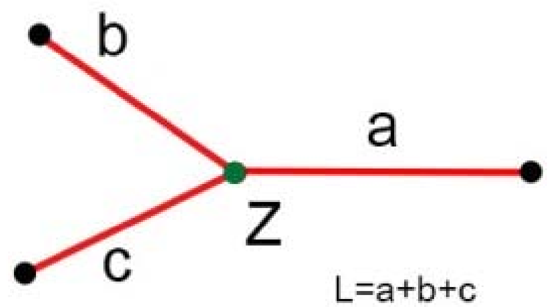
The 3-star graph: a basic graphical motif

$$\psi_n(s) = \cup_{i=1}^3 A_n \frac{\sin k_n(a_i - s_i)}{\sin k_n a_i}$$

Irrationally-related edges (no degeneracies)
Continuous at origin (by construction)

$$E_n = k_n^2/2$$



$$\begin{aligned} L &= a_1 + a_2 + a_3 \\ L_1 &= |a_1 - a_2 - a_3| \\ L_2 &= |a_2 - a_1 - a_3| \\ L_3 &= |a_3 - a_1 - a_2| \end{aligned}$$

Flux continuity at origin yields

$$\cot k_n a_1 + \cot k_n a_2 + \cot k_n a_3 = 0$$

Defining new variables, we get F_{star} = 0,

$$F_{star}(a,b,c) = \frac{1}{4}\left[\cos k_n L_1 + \cos k_n L_2 + \cos k_n L_3 - 3\cos k_n L\right]$$

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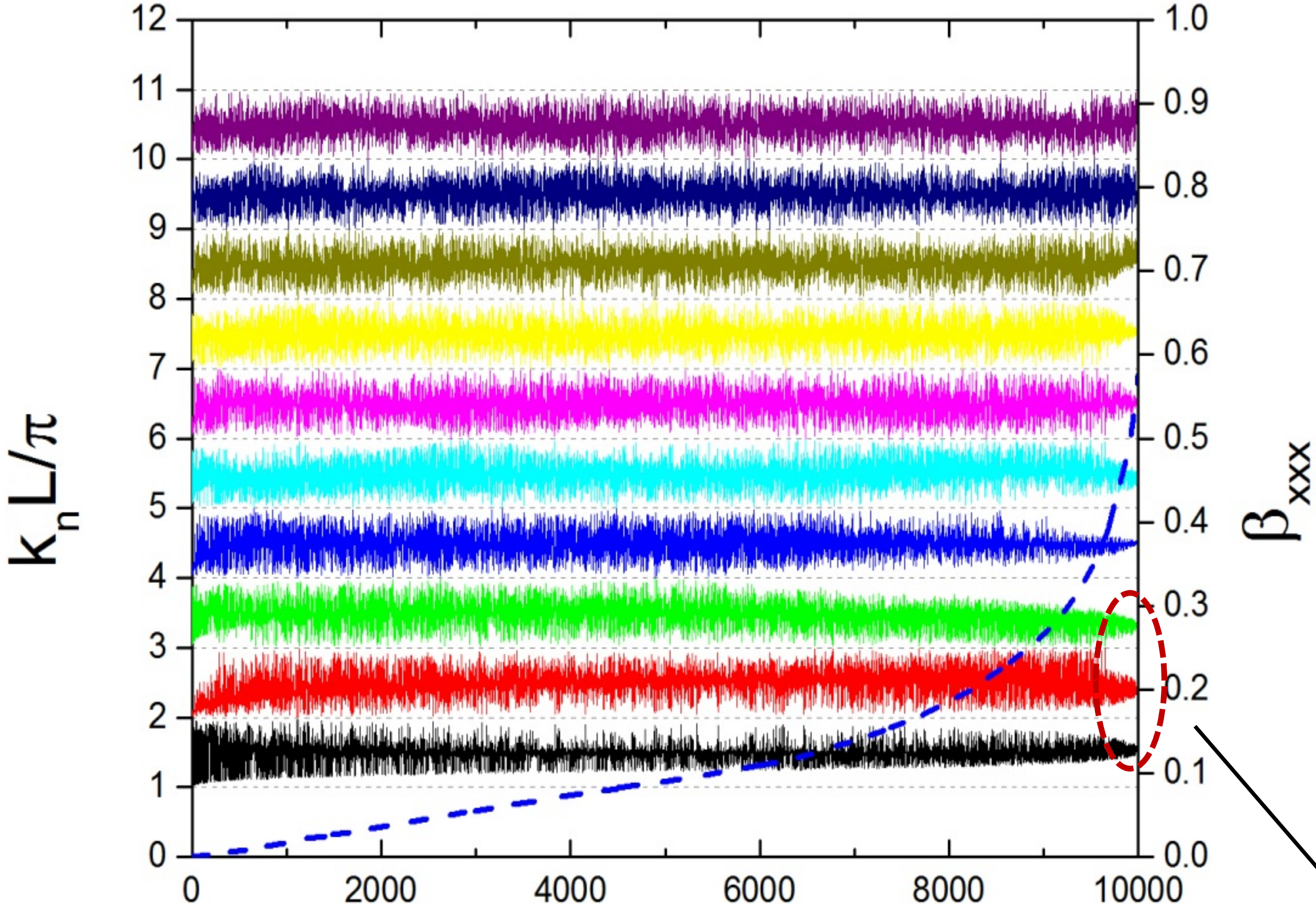
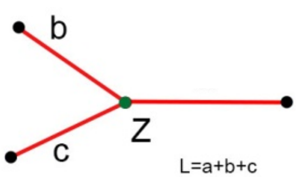
Spectral scaling as β_{xxx} approaches its maximum



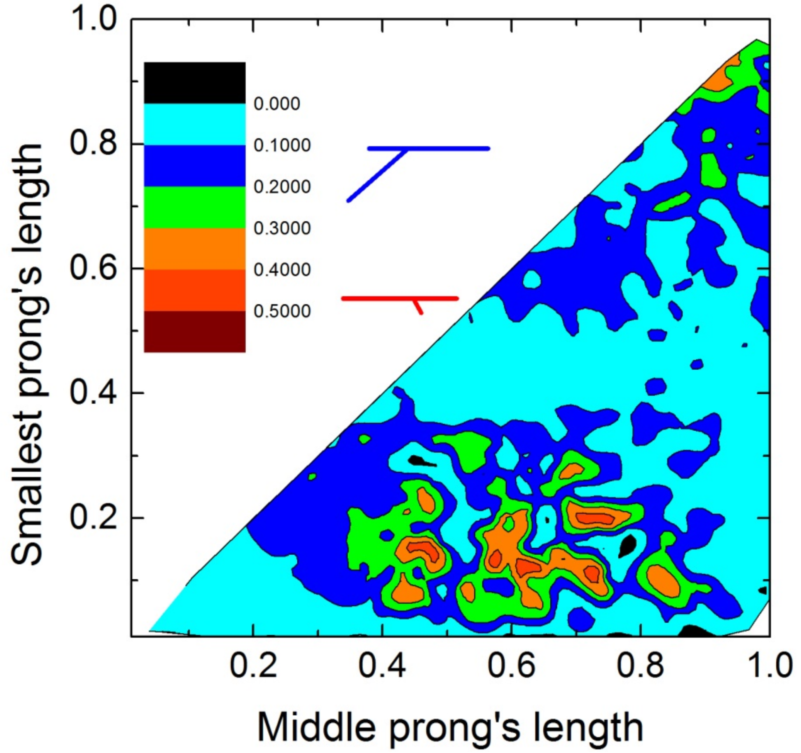
Monte Carlo run #

Note convergence to fixed values at max β_{xxx}

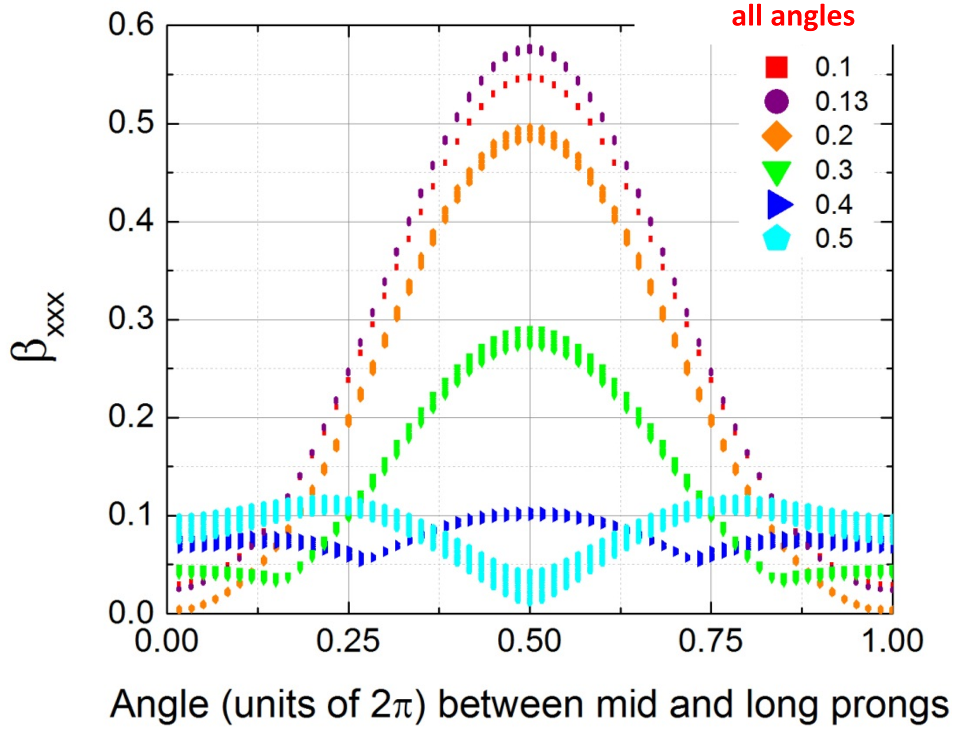


Geometrical properties of the 3-star topology

Maximum possible β_{xxx}



short prong length, all angles



Long prong length = 1
Mid prong length = 0.6

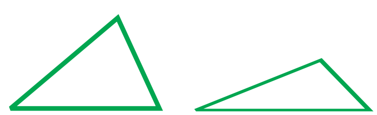
Origin of geometrical and topological effects

$$x_{nm} \equiv \langle \psi_n | x | \psi_m \rangle = \sum_{k=1}^{E} \int_k dx_k \; x^k \phi_n^{k*}(x_k) \phi_m^k(x_k) = \sum_{k=1}^{E} \cos\theta_k K_{nm}^k$$

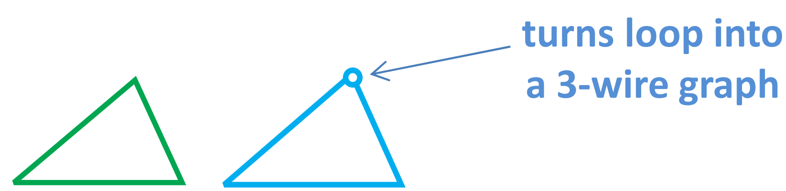
$$\beta_{xxx} \sim \sum_{i,j,k} (\cos\theta_i \cos\theta_j \cos\theta_k) \times \sum_{n,m}{}' \frac{K_{0n}^i \bar{K}_{nm}^j K_{m0}^k}{E_{n0} E_{m0}}$$

Shape-dependent (geometrical)

Mode-dependent (topological)



Identical states & energies



Identical shapes only

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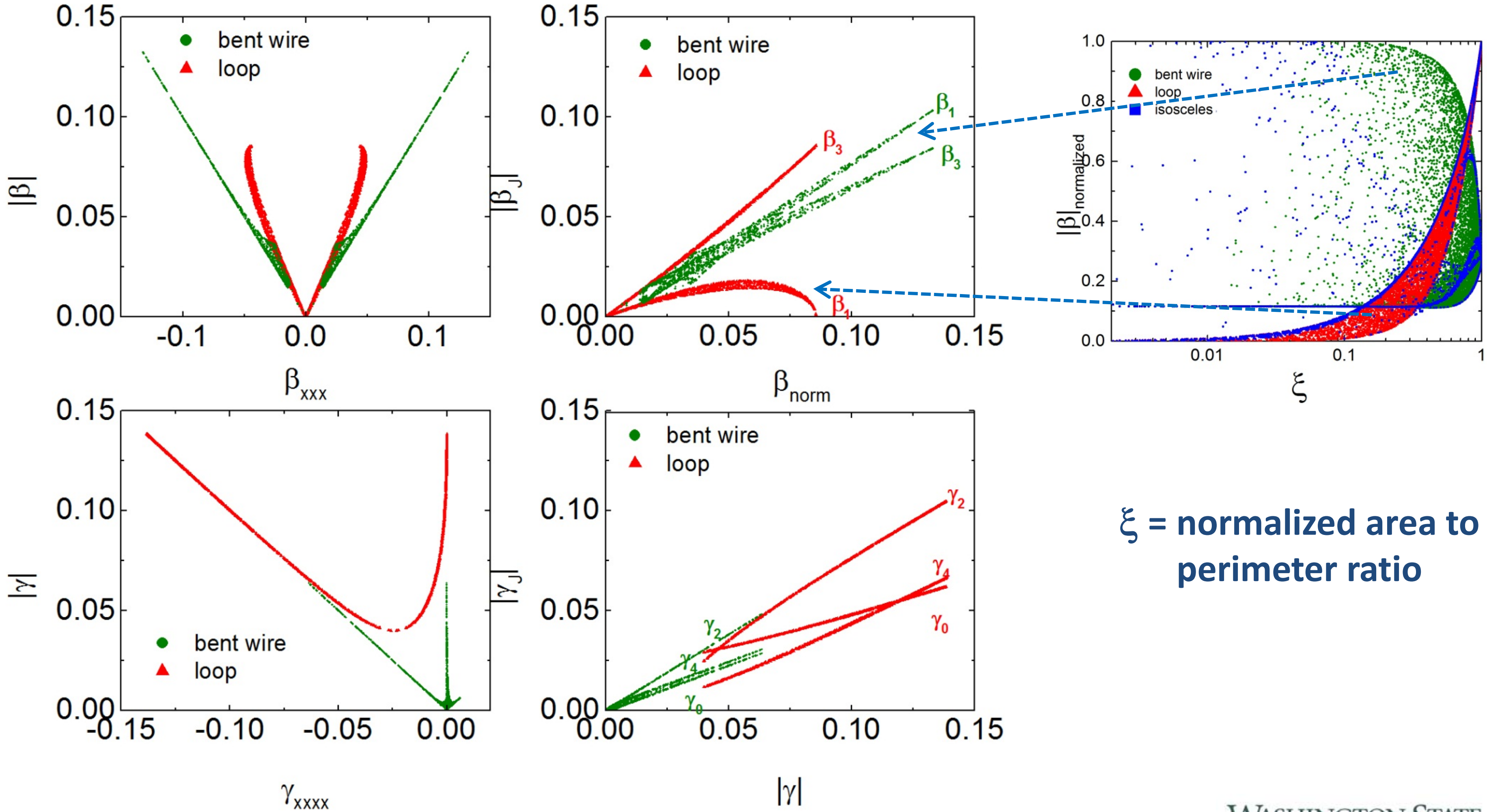
Topological enhancement in triangle graphs



ξ = normalized area to perimeter ratio

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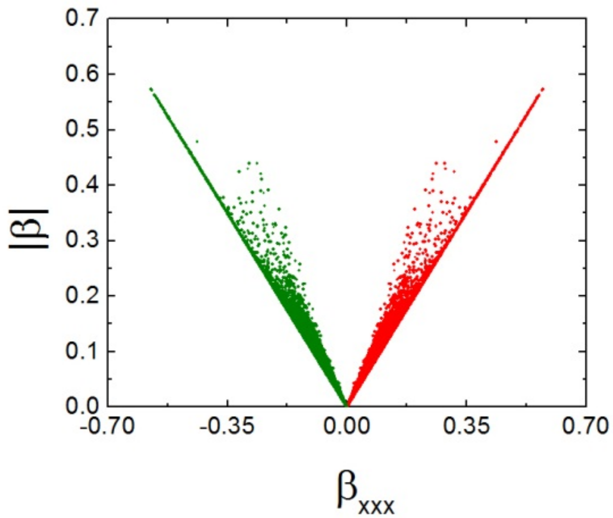
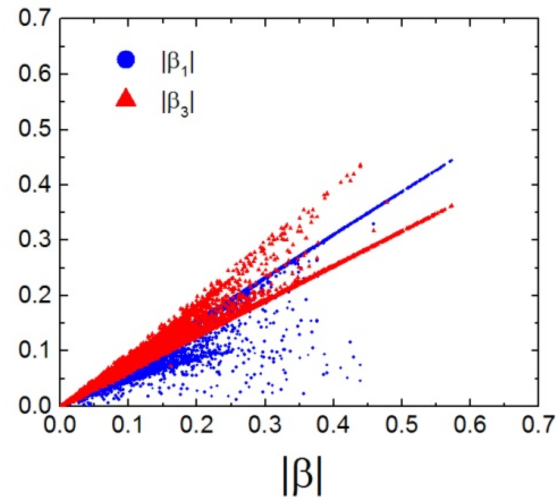
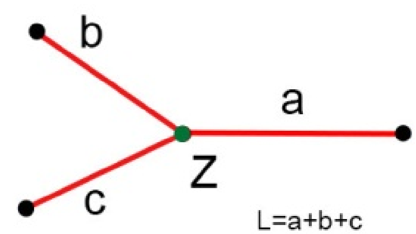
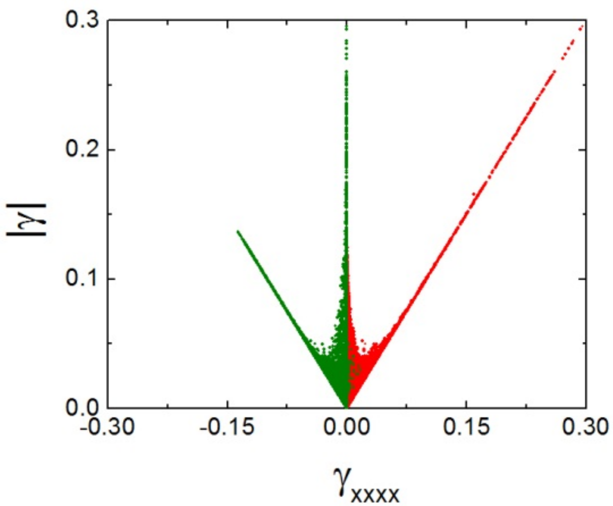
3-star spherical tensors and tensor norms

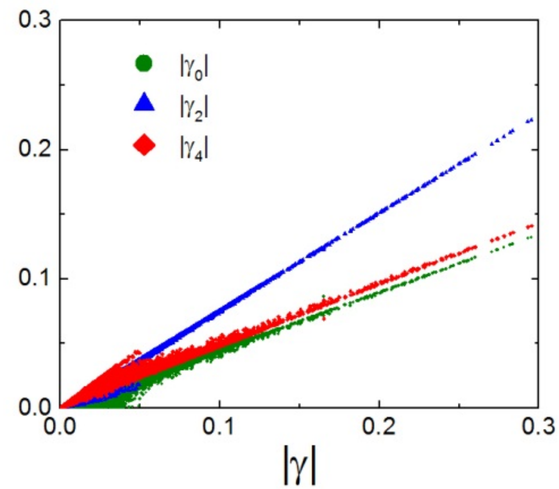




J=1 vector component dominates at max β_{xxx}





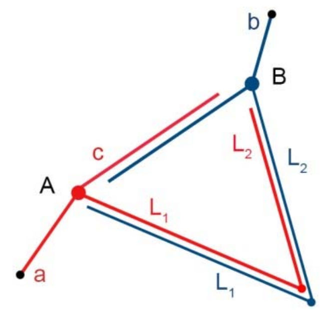


J=2 vector component dominates at max γ_{xxxx}

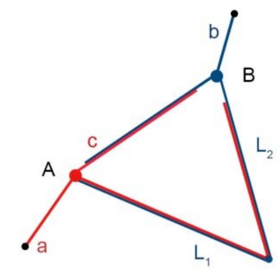
Concept of a graphical motif*

$$
\begin{aligned}
\phi_n^a(s_a) &= A_n \frac{\sin k_n\,(a-s_a)}{\sin k_n a} \\
\phi_n^b(s_b) &= B_n \frac{\sin k_n\,(b-s_b)}{\sin k_n b} \\
\phi_n^c(s_c) &= \left[B_n \frac{\sin k_n s_c}{\sin k_n c} + A_n \frac{\sin k_n (c-s_c)}{\sin k_n c} \right] \\
\phi_n^d(s_d) &= \left[B_n \frac{\sin k_n s_d}{\sin k_n d} + A_n \frac{\sin k_n (d-s_d)}{\sin k_n d} \right]
\end{aligned}
$$

Two 3-stars



Bullgraph



$d = L_1 + L_2$

Flux conservation at each vertex:

$$
A_n \left[\cot(k_n a) + \cot(k_n c) + \cot(k_n d)\right] = B_n \left(\csc(k_n c) + \csc(k_n d)\right)
$$

$$
B_n \boxed{\left[\cot(k_n b) + \cot(k_n c) + \cot(k_n d)\right]} = A_n \left[\csc(k_n c) + \csc(k_n d)\right]
$$

Net flux from star vertex: A "motif"

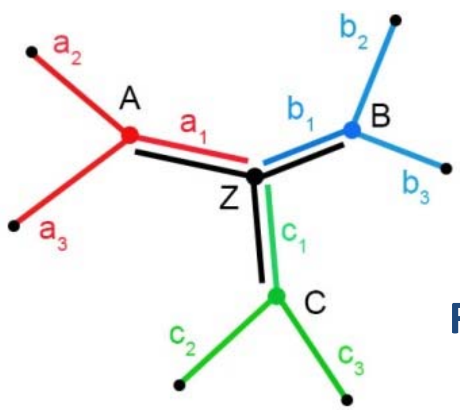
Cross-multiply and rationalize:

$$
\begin{aligned}
F_{bull}(a,b,c,d) &= F_{star}(a,c,d)\,F_{star}(b,c,d) \\
&- \sin k_n a \sin k_n b \left(\sin k_n c + \sin k_n d\right)^2
\end{aligned}
$$

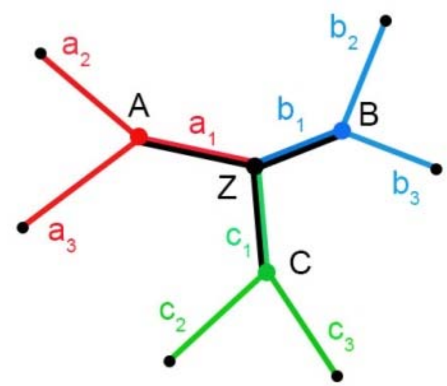
"Scaling and universality in nonlinear optical quantum graphs containing star motifs," R. Lytel, S. Shafei, & M. Kuzyk, arXiv:1305.4334 (2013).

Solve complex graphs by inspection

Four 3-stars



Snowflake graph



Flux conservation at each vertex

$$
\begin{aligned}
A_n F_{star}(a_1, a_2, a_3) &= Z_n \sin k_n a_2 \sin k_n a_3 \\
B_n F_{star}(b_1, b_2, b_3) &= Z_n \sin k_n b_2 \sin k_n b_3 \\
C_n F_{star}(c_1, c_2, c_3) &= Z_n \sin k_n c_2 \sin k_n c_3 \\
Z_n F_{star}(a_1, b_1, c_1) &= A_n \sin k_n b_1 \sin k_n c_1 \\
&+ B_n \sin k_n a_1 \sin k_n c_1 \\
&+ C_n \sin k_n a_1 \sin k_n b_1
\end{aligned}
$$

Secular function for snowflake graph

$$
\begin{aligned}
F_{snowflake} &= F_{star}(a_1, a_2, a_3) F_{star}(b_1, b_2, b_3) F_{star}(c_1, c_2, c_3) F_{star}(a_1, b_1, c_1) \\
&- F_{star}(a_1, a_2, a_3) F_{star}(b_1, b_2, b_3) \sin k_n a_1 \sin k_n b_1 \sin k_n c_2 \sin k_n c_3 \\
&- F_{star}(a_1, a_2, a_3) F_{star}(c_1, c_2, c_3) \sin k_n a_1 \sin k_n c_1 \sin k_n b_2 \sin k_n b_3 \\
&- F_{star}(b_1, b_2, b_3) F_{star}(c_1, c_2, c_3) \sin k_n b_1 \sin k_n c_1 \sin k_n a_2 \sin k_n a_3
\end{aligned}
$$

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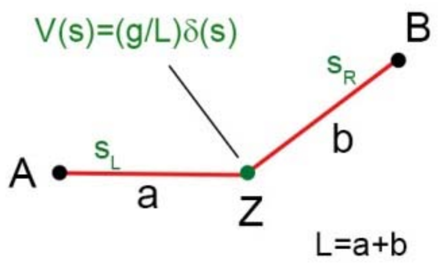
“Dress” a wire (compressed δ atom)*



$$\phi_L(s) = \frac{Z \sin k(a - s_L)}{\sin ka}$$
$$\phi_R(s) = \frac{Z \sin k(b - s_R)}{\sin kb}$$

Secular equation determines eigenvalues for graph

$$0 = F_\delta(g; \omega, kL) = -(1/kL)\left[g(\cos kL - \cos \omega kL) - kL \sin kL\right],\ E \geq 0$$
$$0 = F_\delta(g; \omega, \kappa L) = (i/\kappa L)\left[g(\cosh \kappa L - \cosh \omega \kappa L) + \kappa L \sinh \kappa L\right],\ E < 0$$
$$E_n = k_n^2/2,\ \hbar = m = 1,\ k = \imath\kappa,\ E < 0$$

Finite potential allows a single negative energy state for negative $g<g_c$

$$-\imath x F_\delta(g; \omega, \kappa L) = x^2 \left[1 - \frac{g}{g_c}\right] + O(x^4),\ x \equiv \kappa L,\ g_c = 2/(\omega^2 - 1)$$

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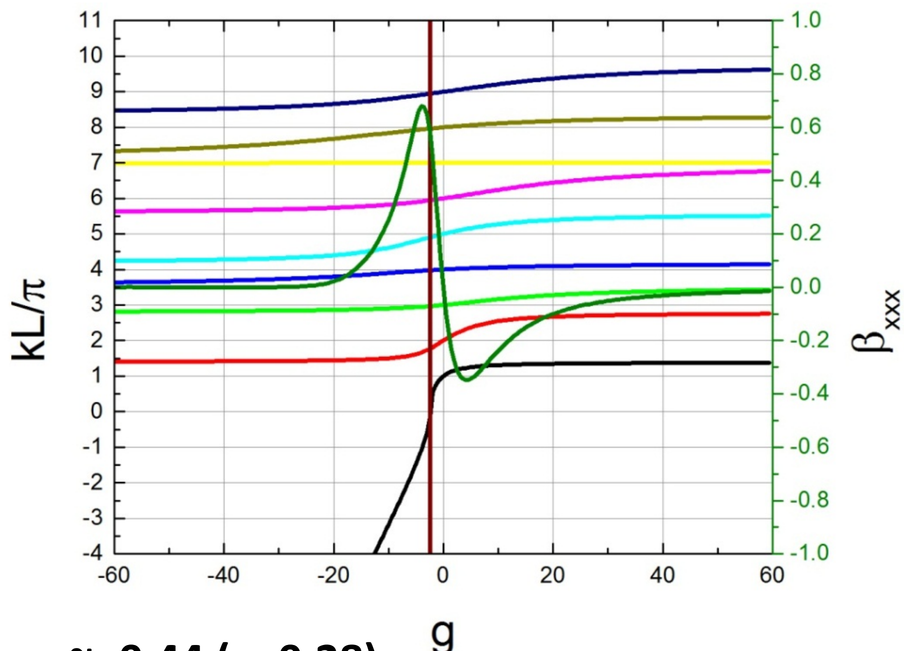
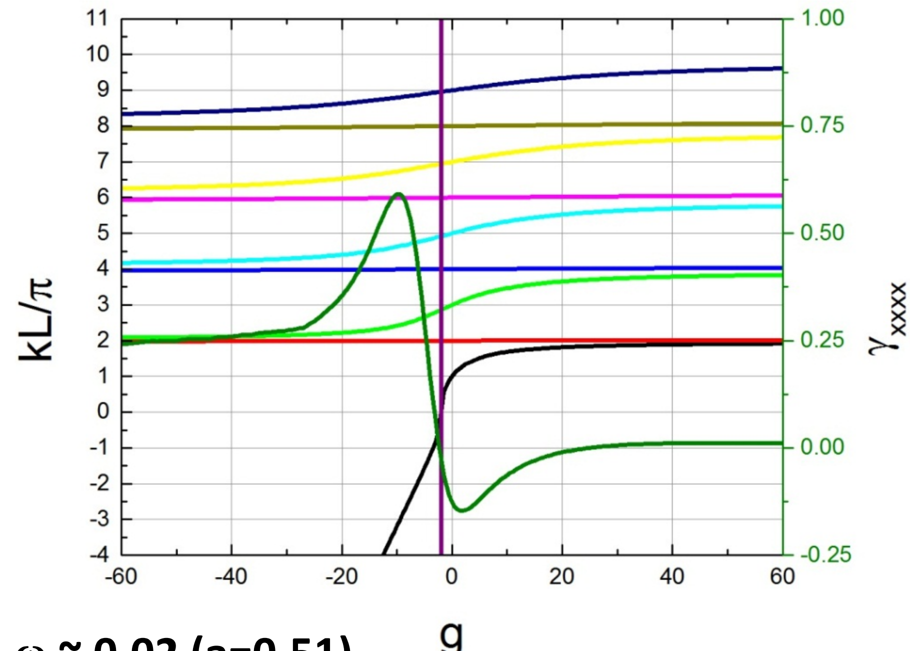
** “Dressed quantum graphs with optical nonlinearities approaching the fundamental limit,” submitted.*

Spectra and hyperpolarizabilities for finite vertex potentials



ω ~ -0.44 (a=0.28)



ω ~ 0.02 (a=0.51)

Positive eigenvalues lie between fixed root boundaries at nπ/L

Topologically-induced spectrum shift when negative energy state appears

Shift induces giant enhancement of nonlinearities.

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"Dressed quantum graphs with optical nonlinearities approaching the fundamental limit," submitted.

Universal scaling & the three level Ansatz*

When β_{xxx} is near its maximum value, only three levels contribute to it

$$\beta_{xxx} = \sum_{n,m}{}' \beta_{xxx}(n,m) = 3^{3/4} E_{10}^{7/2} \sum_{n,m}{}' \frac{x_{0n}\bar{x}_{nm}x_{m0}}{E_{n0}E_{m0}} \rightarrow \beta_{xxx}^{3L},$$

$$\beta_{xxx}^{3L} = 3^{3/4} E_{10}^{7/2} \left(\frac{|x_{01}|^2 \bar{x}_{11}}{E_{10}^2} + \frac{|x_{02}|^2 \bar{x}_{22}}{E_{20}^2} + \left[\frac{x_{01}x_{20}x_{12}}{E_{10}E_{20}} + c.c. \right] \right)$$

$$E = E_{10}/E_{20}, \; E_{n0} = E_n - E_0$$

$$X = x_{01}/x_{01}^{max}, \; x_{01}^{max} = \left(\frac{\hbar^2}{2mE_{10}} \right)^{1/2}$$

$$\boxed{\begin{array}{l} E = \rightarrow 0.5 \\ X = \rightarrow 0.79 \end{array}}$$

** M.G. Kuzyk, Phys Rev Lett 85, 1219 (2000)*

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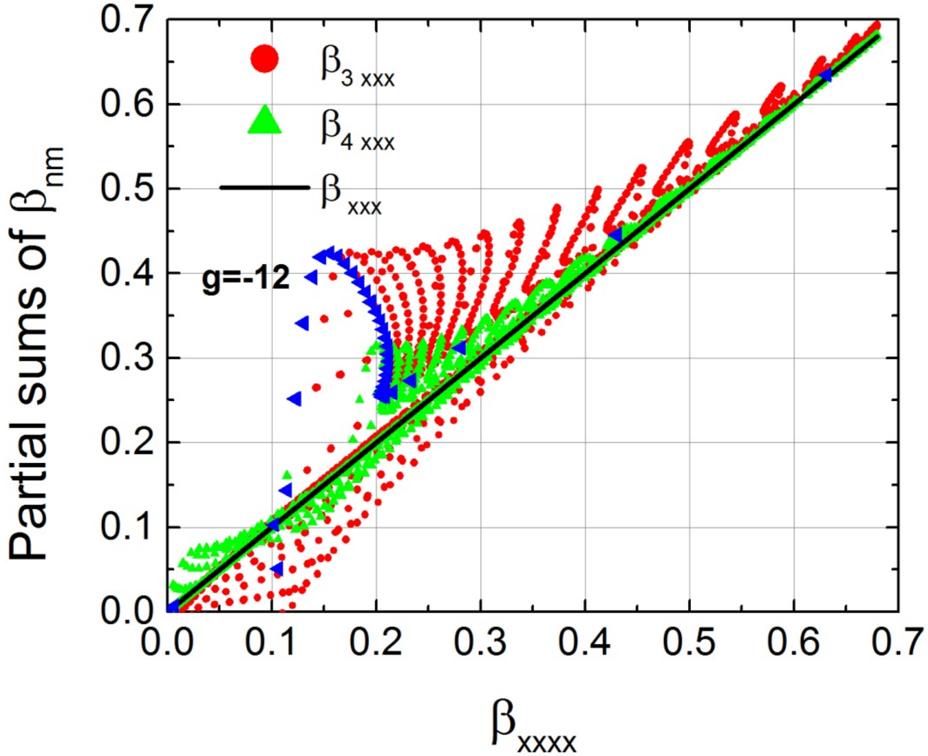
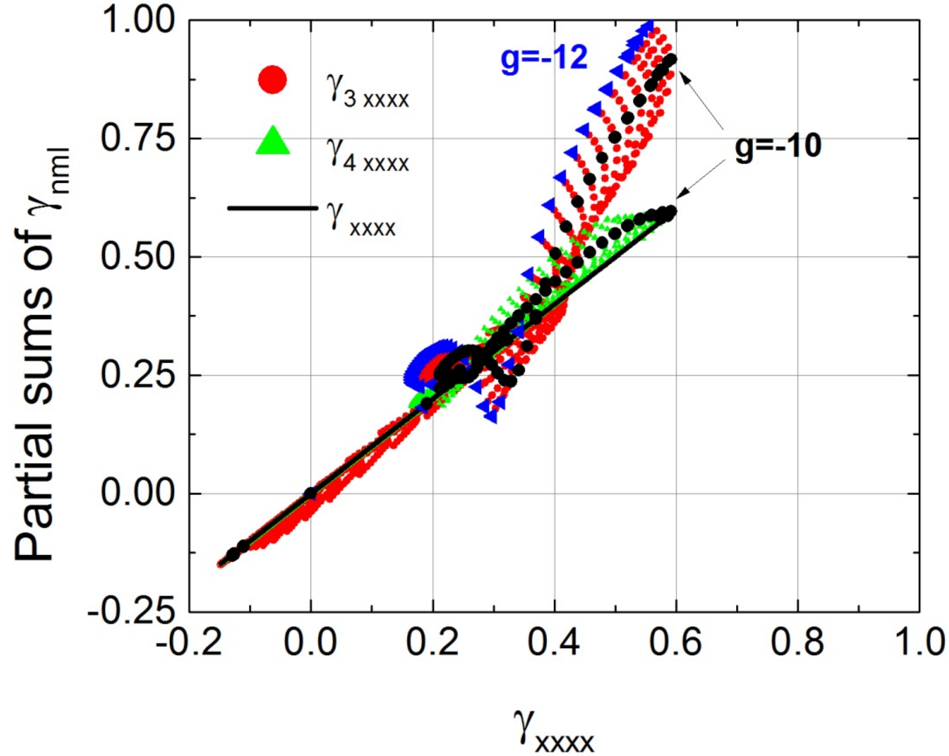
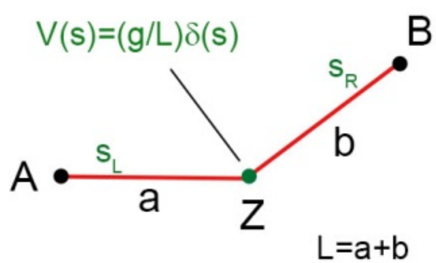
Three- and four-level Ansatz in action

g=-12 to +12.5 in steps of 0.5, each with 200 positions along the wire







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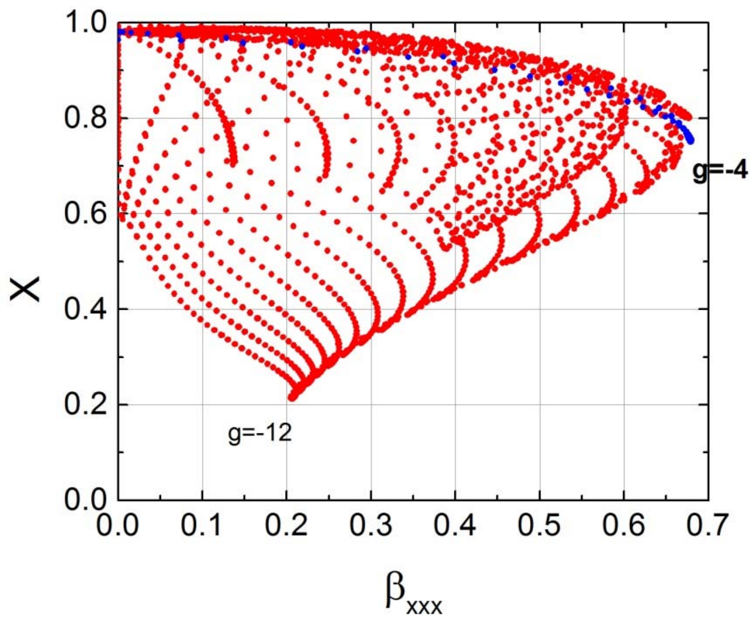
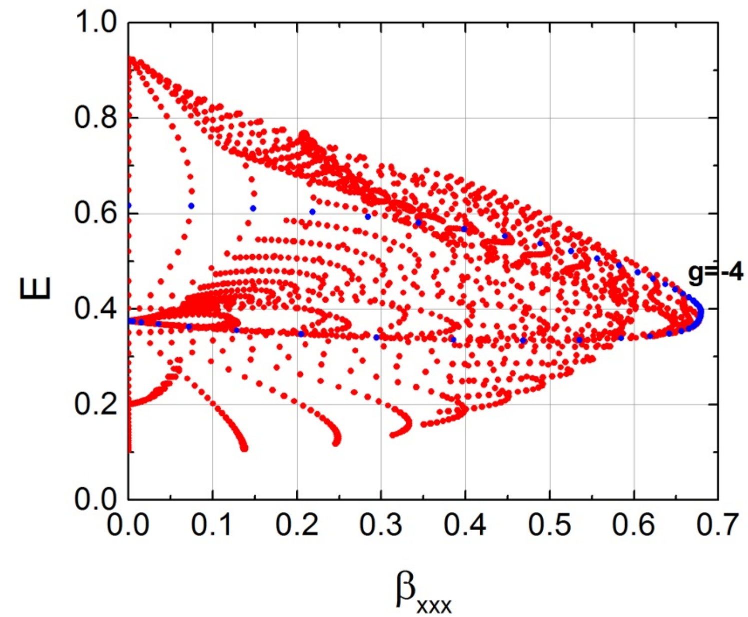
(Near) universal scaling values for X and E

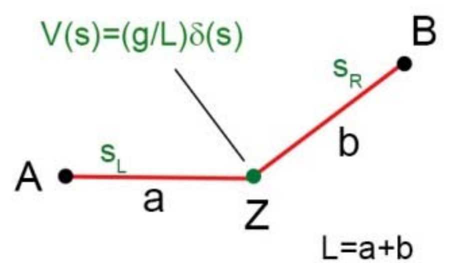




$E = \rightarrow 0.40$

$X = \rightarrow 0.79$

β_{xxx} = 0.68 at g ~ -4



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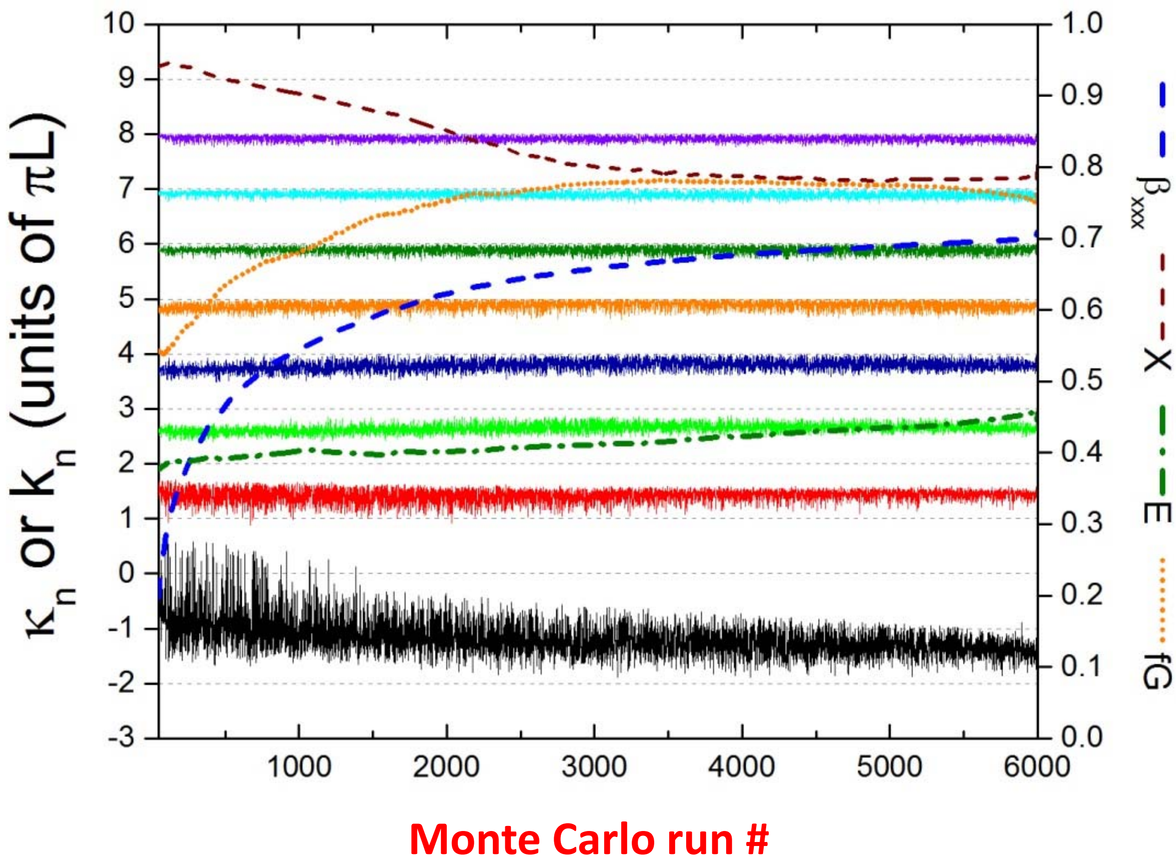
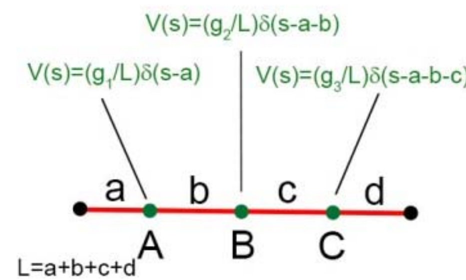
Spectral variation for random δ strengths/locations





$$E = \rightarrow 0.45$$

$$X = \rightarrow 0.79$$

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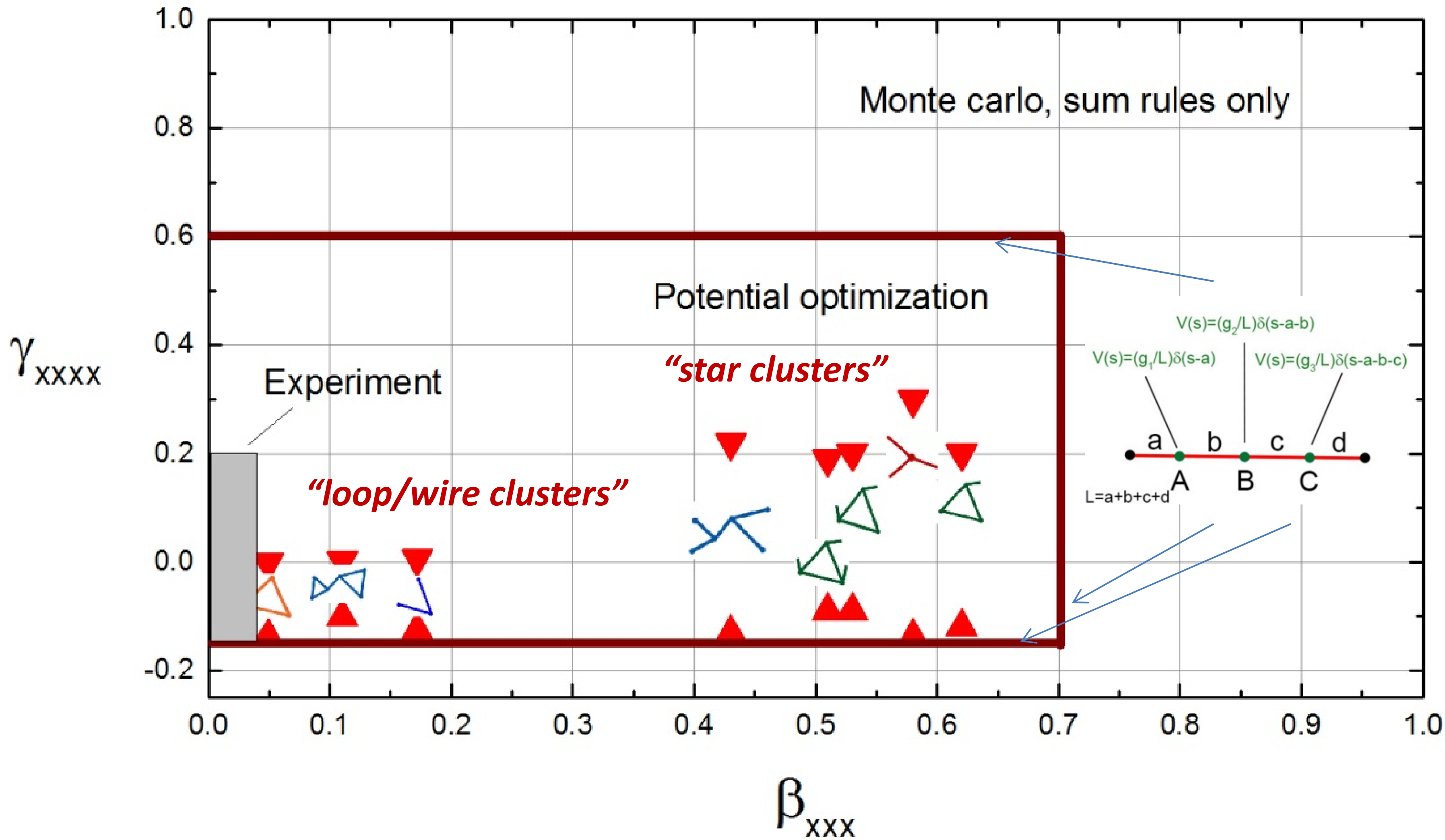
"Dressed quantum graphs with optical nonlinearities approaching the fundamental limit," submitted.

Dressed graphs hit the fundamental limits



Quantum wire networks (quasi-1D graphs)

Topological enhancement of states and spectra for max nonlinearities

General method for solving any graph using motifs

Existence of δ-graphs with $\beta_{max} \sim 0.71$, $\gamma_{max} \sim 0.6$, $\gamma_{min} \sim -0.15$

Possible exception to scaling universality of three-level model

<u>NEXT:</u>

Many-electron model (finite temperature)

Near-resonance phenomena

Make and measure a nanowire with defects

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