PHYSICAL REVIEW B VOLUME 45, NUMBER 7 15 FEBRUARY 1992-I

Strong disorder and the nonlinear susceptibility of conjugated polymers

Daniel Hone and Chandralekha Singh
Department of Physics, University of California, Santa Barbara, California 93106-9530
(Received 5 August 1991)

The effect of quenched randomly distributed bond-breaking defects on nonlinear susceptibilities of conjugated polymers is studied within a tight-binding (Hückel) model. The susceptibility corresponding to third-harmonic generation, $\chi^{(3)}(3\omega)$, is calculated as a function of defect concentration p in chains of length N. Resonant peaks are broadened, as expected, but the overall suppression of $|\chi^{(3)}|$ is weaker than one might assume on the basis of the average segment length between defects.

I. INTRODUCTION

Among the many interesting physical features of conducting polymer chains are their remarkable nonlinear optical properties.[1] In particular, they have unusually large nonlinear susceptibilities,[2,3] even at frequencies too low for real absorption. They also exhibit ultrafast response[4] at the subpicosecond level. These features make the polymers good candidates for fast nonlinear devices.[5,6]

The electrons in these chains occupy two types of orbitals. The σ electrons provide the basic binding to give structural stability to the backbone, but they play very little part in the optical properties we consider here, since their excited states lie at energies well above the frequencies of interest. The mobile π electrons, on the other hand, are characterized by low-lying excited states which dominate the optical properties. Although the linear-chain structure leads, as expected, to relatively large susceptibilities, experimental measurements[7] on long polymers have given low values for the nonlinear coefficients compared to what was anticipated from extrapolation of short-chain results and theoretical predictions.[8] It has been suggested that this discrepancy might be due to a reduction in effective electron delocalization length by the various kinds of disorder present in these systems. In light of this, we here examine theoretically the effects of disorder on these higher-order susceptibilities within a very simple model where quenched random defects completely break the chain, by disrupting π-electron communication. In future publications we will extend consideration to more general types of disorder, including the introduction of annealed defects.

The optical properties are particularly sensitive to disorder,[9,10] because they are determined by the electric dipole matrix elements and by the electronic energy spectrum, particularly the energy gap (Δ) created by the Peierls distortion.[11] The transition dipole matrix element is effectively proportional to the overlap length of the electronic states involved, a quantity which decreases as disorder increasingly localizes the electronic states. The Peierls instability, and therefore the gap, is also diminished by disorder (stretch alignment of polyacetylene has raised[12] the gap from 1.9 to 2.3 eV, for example), which, moreover, can actually create electronic states within the gap[13]—e.g., of polaron or soliton character. Though these considerations hold for optical response generally, it should be noted that higher-order nonlinear susceptibilities involve larger numbers both of matrix elements between different states and of energy denominators which depend on the band gap. Then we expect particularly strong influence of disorder on these nonlinear responses.

For the quasi-one-dimensional chain polymers, the effect of disorder, as always, is much more drastic than it is in higher dimensions. In one dimension there is no way to go around or to avoid a defect, and localization effects are strong. Even complete destruction of electronic communication between segments of a polymer can be effected by breaking a single link—e.g., by a suitable rotation of one monomer relative to the next.

In conjugated polymers the potential kinds of conformational and electronic disorder and defects depend on the type of polymer, its environment, and the way it has been processed. They include various kinds of charged impurities,[13–16] rotations about bonds[17–19] or bending of the backbone, interchain couplings (including cross links), solvent interactions for polymers in solution,[20] sp^3 defects[21] (the local introduction of an additional bonding orbital, which then eliminates the mobile π orbital), thermal fluctuations,[22] and end effects.[9] Some of these, such as rotations about bonds or polymer interaction with the solvent, may dominate in solution, while certain other, including interchain interactions, may be more important in the solid state.

Since second-order nonlinear responses vanish in a centrosymmetric system, one often concentrates on the third-order susceptibilities, notably the third-harmonic generation, of the production of light of frequency 3ω from incident radiation of frequency ω. In this paper we will explicitly limit consideration to this response function.

In the next section we present a calculation of the effect of randomly distributed bond breaks on third-harmonic generation within a simple model. The final section is devoted to discussion and conclusions.

II. MODEL AND CALCULATION

As a first approach to exploring the effect of disorder we consider the simplest case, where defects break completely the π-electron transport along the chain. Then the individual segments between the breaks act as independent chains. We take a quenched random distribution of breaks, characterized only by the defect concentration and length of the chains in which the defects are found. Then the statistical distribution of breaks can be dealt with analytically. Annealed disorder, incorporating defect energetics, must be treated separately.

Consider a monodisperse sample of polymer chains with N identical units connected by bonds susceptible to breaking [the unit, e.g., might be a double-bonded carbon pair, as in $(\mathrm{CH})_x$, or an aromatic ring for polythiophene]. We fix the defect concentration p, the probability of having a break at each bond. Then the system is characterized by $\bar{n}_{Np}(l)$, the average number of segments of length l per chain. The susceptibility of interest, $\chi(l)$ (in this case, third-harmonic nonlinear susceptibility), is evaluated numerically for all accessible values of length l. Then we can compute the average susceptibility per chain $\bar{\chi}^{(3)}(N)$ as

$$\bar{\chi}^{(3)}(N)=\sum_{l=1}^{N}\bar{n}_{Np}(l)\chi(l)\ . \qquad (1)$$

To calculate $\bar{n}_{Np}(l)$, we first note that the probability of having m breaks in an open chain N units long, if the probability of having a break between a given pair of neighboring units is p, is simply given by the binomial distribution

$$f_{Nmp}=\left[\begin{matrix}N-1\\ m\end{matrix}\right]p^{m}(1-p)^{N-m-1}\ . \qquad (2)$$

We denote by $P_N^m(l)$ the probability of having a segment of length l, given that there are m defects, in the chain N units long. Then

$$\bar{n}_{Np}(l)=\sum_{m=0}^{N-1}(m+1)f_{Nmp}P_N^m(l)\ , \qquad (3)$$

where the factor $(m+1)$ is the number of segments of a chain with m breaks.

Finally, the calculation of $P_N^m(l)$ is a standard statistical distribution problem. The fractional number of segments with length l is identical to the fraction of all first segments (the segments nearest to the chain ends) with that length. This, in turn, is the ratio of the number of ways of segmenting the remaining $(N-l)$ units of the chain into m pieces, to the number of ways of segmenting the full chain into $(m+1)$ pieces:

$$P_N^m(l)=\frac{\left[\begin{matrix}N-l-1\\ m-1\end{matrix}\right]}{\left[\begin{matrix}N-1\\ m\end{matrix}\right]}\ . \qquad (4)$$

This analysis implies at least a single break $(m\geq 1)$, but the remaining case $(m=0)$ is simply included: $P_N^0(l)=\delta_{lN}$ and $\bar{n}_{Np}(N)=(1-p)^{N-1}$.

The sum over m in Eq. (3) can be done in closed form:

$$\begin{aligned}\bar{n}_{Np}(l)-(1-p)^{N-1}\delta_{lN}&=\sum_{m=1}^{N-l}(m+1)\left[\begin{matrix}N-l-1\\ m-1\end{matrix}\right]p^{m}(1-p)^{N-m-1}\\ &=p(1-p)^{l-1}\left[2+p\frac{d}{dp}(p+q)^{N-l-1}\right]_{q=(1-p)}\\ &=p(1-p)^{l-1}[2+p(N-l-1)]\ ,\end{aligned} \qquad (5)$$

an exponentially decreasing function of l. Finally, the average $\bar{\chi}^{(3)}(N)$ for an ensemble of chains of length N is given by Eq. (1).

We now turn to the calculation of the susceptibility $\chi(l)$, which differs from earlier studies only in that we allow the finite-chain configuration to relax. These end effects are substantial only when the chain length is less than 15–20 units, and such small chain segments, which have very small susceptibilities, do not contribute significantly to the overall $\bar{\chi}^{(3)}(N)$ for $N>50$ [we reemphasize that 50 "units" does not in general imply 50 single carbon atoms along the backbone; e.g., in $(\mathrm{CH})_x$ there are two carbon atoms per unit]. Nevertheless, we briefly review the calculation in order to discuss the various physical processes that contribute to the nonlinear response. The expression for the third-order susceptibility at zero temperature (temperature plays a negligible role, since it is much smaller than the gap) from standard perturbation theory can be written as[8,23]

$$\begin{aligned}\chi^{(3)}(3\omega;\omega,\omega,\omega)=&\,e^4\sum_{n\neq g}\sum_{m\neq g}\sum_{l\neq g}f_{gn}f_{nm}f_{ml}f_{lg}\left[\frac{1}{(E_{ng}\pm3\omega)(E_{mg}\pm2\omega)(E_{lg}\pm\omega)}+\frac{1}{(E_{ng}\pm\omega)(E_{mg}\mp2\omega)(E_{lg}\mp\omega)}\right]\\ &-e^4\sum_{n\neq g}\sum_{m\neq g}f_{gn}f_{ng}f_{gm}f_{mg}\left[\frac{1}{(E_{ng}\pm3\omega)(E_{ng}\pm\omega)(E_{mg}\pm\omega)}+\frac{1}{(E_{ng}\pm\omega)(E_{mg}+\omega)(E_{mg}-\omega)}\right]\ .\end{aligned} \qquad (6)$$

Here f_{ij} is the electric dipole matrix element between states i and j, and E_{ij} is the energy difference between those states. The upper and lower set of signs in each product are to be included independently in the overall sum.

To progress further we need an explicit model. We take the simplest form which incorporates the essential physics: electron mobility which depends on the chain configuration and an elastic configurational energy. We modify the standard Su-Schrieffer-Heeger[24] (SSH) tight-binding Hamiltonian for polyacetylene only in allowing the bonds to relax independently (so as to include end effects appropriate to open chains). A single band of π electrons is described by spatially localized Wannier functions with an effective hopping between nearest-neighbor units (again, not necessarily single carbon sites). In dimensionless form,

$$\mathcal{H}/t_0=\sum_{n,\sigma}(1-u_n)(c^\dagger_{n+1\sigma}c_{n,\sigma}+c^\dagger_{n,\sigma}c_{n+1,\sigma})+g\sum_{n}u_n^2 \ , \tag{7}$$

where t_0 is the hopping matrix element for a structurally rigid uniform chain. For numerical calculations we arbitrarily choose the reduced (dimensionless) stiffness constant g to be 0.9, a value appropriate to $(\mathrm{CH})_x$; it reflects the size of electron-phonon coupling, as well as the intrinsic bond elastic stiffness. The subscript n labels the sites, and u_n is the fractional change in bond length between the sites n and $n+1$ from that of the uniform chain. The creation and annihilation operators $c^\dagger_{n,\sigma}$ and $c_{n,\sigma}$ refer to the above Wannier states at site n with spin σ.

Within the adiabatic approximation of Eq. (7) (no atomic dynamics), there are no instantons, which have been proposed[25] as an important mechanism in nonlinear optical processes. However, their importance is certainly reduced in short segments where there is not even approximate ground-state degeneracy, and in any case, the focus of the present study is on the impact of disorder. We therefore explore the effects of disorder within this frequently studied approximation, where the displacements u_n are parameters determining a set of one-electron states and eigenvalues whose occupation gives the states and energies in Eq. (6). The first term in that equation is the sum over all third-order virtual transitions where the system never returns to the ground state at any intermediate stage, including the processes shown in Figs. 1(a)–1(c). The only remaining contributions come from diagrams of the form shown in Fig. 1(d), where the creation and annihilation of a given particle-hole pair is repeated twice. Disconnected diagrams such as that shown in Fig. 1(f) do not contribute, since they cancel term by term with processes such as that shown in Fig. 1(e). We restrict ourselves to the half-filled band case, in part for reasons of simplicity. The addition of carriers by electronic doping introduces the familiar topological excitations—solitons, polarons, etc.—with accompanying states within the original Peierls energy gap. It would surely be inappropriate to treat the corresponding spatially inhomogeneous state within a model of quenched random break defects which ignores the important energetics of the excess charge-carrier distribution. Moreover, the consequent reduction or elimination of the gap introduces absorption processes at undesirably low frequencies. In fact, for these reasons experiments on third-harmonic generation in these materials have also largely been restricted to undoped systems. We can then invoke the electron-hole symmetry of the half-filled band: There is a complementary set of processes related to those shown by the interchange of corresponding electrons and holes, whose contributions are identical to those of the processes shown.

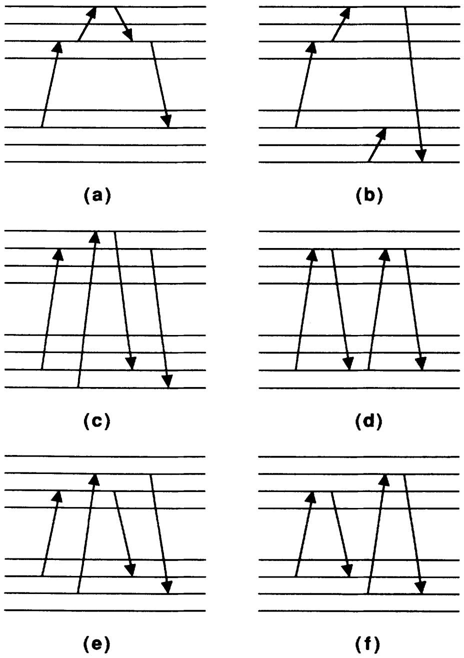

FIG. 1. Dominant types of transitions contributing to $\chi^{(3)}$ [Eq. (6)] from electron states near the gap (at the center of the horizontal energy levels shown in each diagram). Each process proceeds from left to right.

We make several approximations in the calculation of the matrix elements that enter Eq. (6). Formally, the results are for a sample of chains fully aligned with each other and with the applied electric field; we ask for the completely diagonal component of the fourth-rank susceptibility tensor χ_{xxxx}. The extension to a distribution of angles θ between the independent segments and incident electric field is trivial: There is a factor of $\cos(\theta)$ for the corresponding matrix elements (and a similar factor for the outgoing wave at 3ω), and a suitable average can be taken over the distribution. The individual segments *are* assumed to be linear; orientational departures from this, such as local coiling of the chain, must be treated separately and explicitly. Finally, we have taken the distance parameter x of the dipole operator to be proportional to the number of units along the chain—i.e., we have not included the effects of bond-length relaxation in this operator. The changes in bond length are typically of order a few percent, and the effect on the susceptibility is of this same order.

In the half-filled band systems, the first excitation from the ground state necessarily will be across the Peierls gap. For this interband transition, the dipole matrix element is approximately independent of the length of the chain (roughly the matrix element of x between two plane waves, each of wave vector G, but out of phase). But for the intraband transitions, which connect states corresponding to plane waves with wave vectors differing by $(\Delta k)\sim 1/l$, the normalized matrix elements $\sim 1/l(\Delta k)^2 \sim l$, proportional to the length over which the electron wave function is delocalized. The energy denominators, which for the dominant contributions are each approximately equal to the gap Δ, also depend on segment length l. Initially, for short chains, we find that Δ^{-1} grows approximately as the square root of l, with an asymptotic approach to a constant value as l increases. Of course, $\bar{\chi}^{(3)}(N)$ must become extensive ($\propto N$) for large enough N. Mathematically, this develops, as the electron states merge into a quasicontinuum, from the cancellation of the matrix elements in the single-electron processes for transitions with and without exchange of fermions. The average susceptibility per unit length, $\bar{\chi}(l)/l$, initially grows approximately as $l^{3.9}$ and ultimately saturates, as we have just discussed. From the above discussion we understand one factor of l from each of the dipole matrix elements and of order 2 more from the energy denominators (and, overall, one is removed by normalization to unit length). This behavior is similar to the results obtained by Heflin *et al.*[26] who found the initial exponent to be between 3.7 and 4.4 in their quantum-chemical calculations of *cis* and *trans* forms, respectively, of polyene oligomers. A recent independent calculation by Shuai and Brédas[6] of $\chi^{(3)}$, using an approach similar to ours, but including energy-dependent excited-state lifetimes, finds the value 3.32. The results obtained by Yu *et al.*[8] are qualitatively similar, but their initial exponent is again smaller (~ 3), which may be attributable in these short chains to the differential relaxation near chain ends, which we have included in determining energy eigenvalues. Their saturation value, however, is similar to ours (and for the long chain, where saturation has occurred, the end effects are negligible). As these authors have pointed out, the quantitative agreement with experiment, for polyene chains up to about 20 backbone carbons, is very good.

III. RESULTS AND DISCUSSION

The susceptibility per chain unit, $\bar{\chi}^{(3)}(N)/N$, is plotted in Fig. 2 as a function of N for various defect concentrations. The frequency ω is chosen to be less than one-third of the gap, $\omega < \Delta/3$, so that there is no real absorption. We have only a few representative numerically calculated values of $\chi(l)$; to carry out the sum of Eq. (1) over *all* values of l, we simply interpolate smoothly between them. Since $\bar{n}_{Np}(l)$ falls exponentially and $\chi(l)$ is a monotonically increasing function, the summand of Eq. (1), $\chi(l)\bar{n}_{Np}(l)$, is peaked. If the peak were sharp enough that the sum was dominated by terms with $l \sim \bar{l}$, where $\bar{l} = \sum_l \bar{n}_{Np}(l)$ is the average segment length, then the rapid falloff of $\chi(l)$ with decreasing l, below $l = 50$, would suggest a very substantial reduction in $\bar{\chi}^{(3)}(N)$ with only a few percent of bond-breaking defects: $\chi^{(3)}(N)/N \sim \chi(\bar{l})/\bar{l}$. But with a random distribution of defects, the superlinear dependence of $\chi(l)$ on l strongly weights longer segments, which then make contributions to $\bar{\chi}^{(3)}(N)$ disproportionately large compared to their probability of occurrence. Therefore, substantial reduction of $\bar{\chi}^{(3)}(N)$ from its saturated value comes only with *tens* of percent random breaks. We do note that if the defects are, instead, annealed, the electron delocalization energy promotes regularity of segment size (an effective mutual repulsion between successive breaks), leading to a more highly peaked distribution of lengths l about the average, $\bar{l}$, so that $\bar{\chi}^{(3)}(N)/N$ is more nearly $\chi(\bar{l})/\bar{l} \sim p\chi(1/p)$ and the reduction of $\bar{\chi}^{(3)}(N)$ then is effected at smaller defect concentrations.

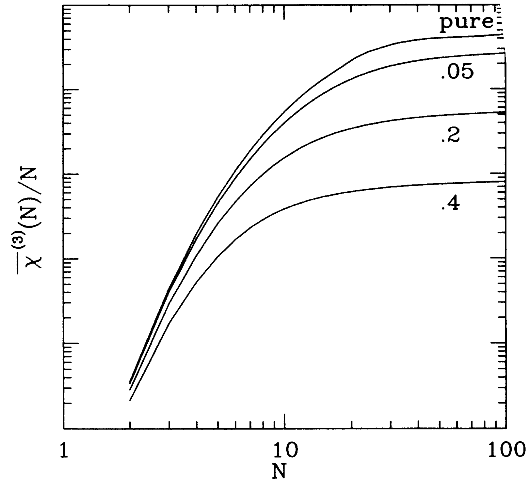

FIG. 2. Average low-frequency third-harmonic generation (THG) susceptibility per monomeric unit, $\bar{\chi}^{(3)}(N)/N$, as a function of total chain length N. The defect concentration p labels the curves.

In Fig. 3 the saturation value $\chi_{\text{sat}}(p)$ of the susceptibility per chain and the "saturation length" N_{sat} at which $\bar{\chi}^{(3)}(N)/N$ reaches a value $(1-1/e)\chi_{\text{sat}}$ are plotted as functions of defect concentration p. We see that $\chi_{\text{sat}}(p)$ has an approximately exponential dependence on p, decreasing from 26 for $p = 0.05$ to 0.8 for $p = 0.40$. N_{sat} decreases from 26 to 14 over this same range of p. The strong dependence of χ_{sat} on p is the expected sensitivity to the electron localization length emphasized above.

We can also look beyond the low-frequency region ($\omega \ll \Delta/3$) to examine the effects of disorder when real absorptive transitions become possible. However, it is then impractical to interpolate smoothly between a few

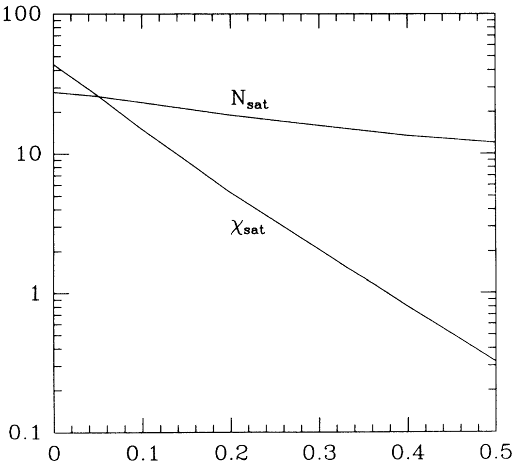

FIG. 3. Saturation value (long-chain limit) of average THG susceptibility χ_{sat} and chain length N_{sat}, where it drops to $1/e$ of that value, as functions of defect concentration p.

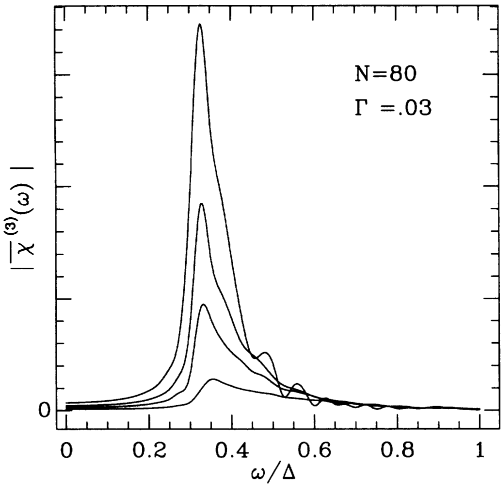

FIG. 4. Absolute magnitude of average THG susceptibility as a function of frequency for chain length $N=80$ and excited-state lifetime parameter $\Gamma=0.03$. From highest to lowest peaks, the curves correspond to defect concentrations $p=0$, 0.05, 0.10, and 0.20.

numerically calculated values of $\chi(l)$ for each frequency ω. In the neighborhood of the interesting resonances, the susceptibility is a sensitive function of chain length (at least for relatively small lengths), as the energy levels which determine those resonances themselves change with this parameter. Hence we have numerically inserted a random distribution of chain breaks with concentration p in an ensemble of chains with fixed total length N to obtain a statistical measurement of $\bar{\chi}^{(3)}(N)$ for a range of frequencies. To avoid artificial divergences we introduce an imaginary part to the excited-state energies in Eq. (6): $E_{ng} \rightarrow E_{ng} + i\Gamma$. Numerically, we choose as the damping factor $\Gamma=0.03$, where we recall that in these dimensionless energy units the gap Δ is of order unity, and so the scale is approximately that of electron volts. Then the model energy-level width Γ is of the order of an inverse phonon frequency, a lower limit to the physical value as set by lattice relaxation processes. Moreover, it is relatively small compared to the width of the predicted resonances and does not artificially distort their shape; we note that this value is comparable to that which has been chosen[8,27] by others. The results for $|\bar{\chi}^{(3)}(N)|$, for various defect concentrations p, plotted in Fig. 4, show a significant decrease in the susceptibility near the peaks at $\omega=\Delta/2$ and $\Delta/3$. For large defect-free samples, our results are similar to those of Yu *et al.*[8] and Wu,[28] with a true three-photon absorption peak at one-third the gap. A second peak at half the gap, observed experimentally,[29] disappears with increasing chain length within theories (such as the present one) with constant excited-state lifetimes,[27,30] although a recent theory with energy-dependent lifetimes[31] reproduces it even in the long-chain limit. True two-photon absorption is forbidden in a system with a center of symmetry; this peak is rather the consequence of a large polarizability near $\omega=\Delta/2$. We do see this and other subsidiary structures associated with the spectral discreteness for shorter chains. In any case, with the introduction of break defects, all peaks decrease significantly. In fact, all structure except for the three-photon absorption at $\omega=\Delta/3$ has become unobservable by the time the defect concentration is as large as 5% in a sample with chains of length $N=80$. We understand this as a consequence of the distribution of chain-segment lengths in the disordered system, with a corresponding distribution of electronic energy levels (including gap size), so that sharp structure becomes smeared.

Of course, a realistic polymer sample is polydisperse. The above results are readily extended to incorporate this feature by making a suitable weighted average over the total chain length N.

ACKNOWLEDGMENTS

We are grateful to Dr. Alan Heeger for introducing us to this problem, and to him, Thomas Hagler, and Duncan McBranch for interpretation of the experimental results in this area. We also thank Dr. Philip Pincus, Dr. W. P. Su, and Dr. Alan Konheim for helpful discussions. This work was supported in part by the National Science Foundation under Grant No. DMR-8906783. Computations were performed in part at the San Diego Supercomputing Center.

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