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Local exciton ground states in disordered polymers

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Exciton localization in conjugated polymers with weak conformational disorder is investigated via the Anderson model with Gaussian off-diagonal disorder, σ. We show that a small fraction of the low-energy eigenstates are spatially localized, nonoverlapping, and space filling. We term these states "local exciton ground states" (LEGS). The LEGS exhibit an almost Gaussian density of states, an average localization length $L \sim \sigma^{-2/3}$, and an inhomogeneous optical linewidth $\sim \sigma^{4/3}$. Their transition dipole moments scale with their localization length in a way consistent with a lowest energy excitation confined to a region $\sim O(L)$. The length scale over which the LEGS are confined is an effective low-energy conjugation length or spectroscopic segment. The appendix describes an efficient and accurate technique for calculating the density of states of the Anderson model.

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I. INTRODUCTION

Excitons are the primary excited states of π-conjugated polymers. The length scale over which the exciton center-of-mass retains phase coherence in a disordered polymer defines the exciton coherence or localization length. For polymers with a sufficiently stiff torsional potential, so that true breaks in the π-conjugation caused by negligible neighboring π-orbital overlap do not occur, the exciton localization length defines an effective exciton confinement length (to be defined more precisely later).

Conversely, for polymers with a soft torsional potential—leading to breaks in the π-conjugation—the average length scale between these breaks defines another length scale, which we call the π-conjugation length. The shorter of the π-conjugation length and the exciton confinement length can be regarded as an effective low-energy exciton conjugation length.

Since the exciton conjugation length determines a number of important electronic processes in polymers, including the optical oscillator strength, the resonant exciton transfer integral,[1,2] and the dispersion interactions,[3] a theoretical understanding of the factors that control its length has important practical applications.

In this paper, motivated by the work of ref 4, we consider polymers with stiff torsional potentials [e.g., poly(p-phenylene) (PPP)] so that the thermally induced conformational disorder is a Gaussian random variable. [In a forthcoming publication we will consider polymers with soft torsional potentials [e.g., polythiophene (P3HT)] where there is a bimodal distribution of torsion angles and there exist breaks in the π-conjugation.[5]]

The purpose of the present work is to investigate the concept of "local exciton ground states" (LEGS), first proposed by Malyshev and Malyshev[6] in their work on diagonal disorder in molecular aggregates (and called by them "local ground states"). LEGS were also observed qualitatively in quantum chemistry calculations on PPP reported by Barford and Trembath.[4]

We model exciton delocalization in disordered polymers via the single particle Anderson model with nearest-neighbor off-diagonal disorder. We show that LEGS are locally the lowest excited states. They are spatially nonoverlapping and space filling, and define effective low-energy conjugated (or spectroscopic) segments. They provide a quantitative justification for the Gaussian random disorder model used to describe exciton transport in disordered polymers.[7] Although focused on exciton states in disordered polymers, the work presented here on the spatial correlations and energetic distributions of low lying eigenstates has wider applicability to quantum wires and other one-dimensional systems.

In the next section we present the theoretical model and discuss some of the computational details. (The Appendix describes an efficient numerical method of obtaining linewidths.) In Sec. III we describe and discuss our results.

II. THEORETICAL BACKGROUND

As described in Sec. III of Ref. 4, the center-of-mass motion of a Frenkel exciton through a polymer with conformational disorder can be mapped onto the Anderson model with off-diagonal disorder,

$$H = -\sum_{R=1}^{N-1} t_R(|R\rangle\langle R+1| + |R+1\rangle\langle R|). \qquad (1)$$

The basis state $|R\rangle$ corresponds to a Frenkel exciton on the unit cell at position R. Here $\{t_R\}$ is taken to be Gaussian random variable, with a mean value of t_0 and standard deviation of σ.

As shown in Ref. 4, for thermally induced conformational disorder $\sigma \sim T^{1/2}$ (where T is the absolute temperature). It was also shown that realistic parameters for PPP are $\sigma/t_0 = 0.065$ and $\sigma/t_0 = 0.272$ for singlet and triplet excitons, respectively; the disorder being effectively larger for triplets because of their narrower bandwidth.

H has a complete set of eigenstates $\{|\Psi_i\rangle\}$ and corresponding eigenvalues $\{E_i\}$. Equation (1) is solved for systems of 1000 sites (or repeat units) for up to 5000 realizations of the disorder. In general, we will be interested in the average density of states and the optical absorption of the Anderson model, which we calculate using a highly efficient approach

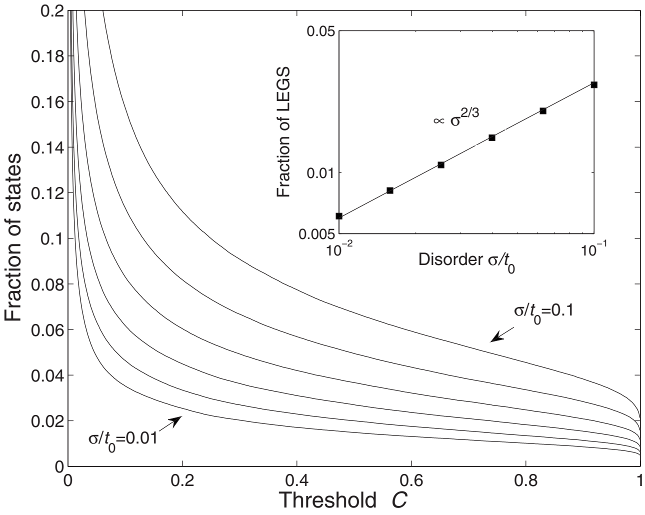

FIG. 1. The fraction of states, x, with a value of the signed-value parameter, α, exceeding C. The values of σ/t_0 shown increase logarithmically, as $10^{-2}, 10^{-1.8}, 10^{-1.6}, \ldots, 10^{-1}$. The inset shows that $x \sim (\sigma/t_0)^{2/3}$ at $C=0.95$. The number of repeat units, N, used was $N=1000$ and each calculation was performed over 500 realizations of the disorder.

(originally proposed by Makhov *et al.*[8–10] for the case of diagonal disorder and described further in the Appendix).

The properties of Eq. (1) have been extensively studied in one and higher dimensions.[11] It is well established that in one dimension disorder causes exponential localization of the particle wave function[12] (see Ref. 13 for a review). For future purposes, we define the exciton localization length as the spread of the exciton center-of-mass wave function,

$$L = 2R_{\mathrm{rms}} \equiv 2\sqrt{\langle R^2\rangle - \langle R\rangle^2}, \tag{2}$$

where

$$\langle R^n\rangle = \sum_R |\Psi(R)|^2 R^n, \tag{3}$$

and $\Psi(R)=\langle R|\Psi\rangle$.

Following Malyshev and Malyshev,[6] we now define a "signed-value" parameter, α,

$$\alpha = \left| \int |\Psi(R)|\Psi(R)dR \right|, \tag{4}$$

such that $\alpha=1$ for the true lowest excited (nodeless) state. As described in the next section, a value of α greater than or equal to $\sim$0.95 is an appropriate definition of a LEGS.

III. RESULTS AND DISCUSSION

Figure 1 shows the fraction of states whose signed-value parameter α exceeds a threshold C. The fraction of such states grows rapidly from zero to an almost constant value as the threshold is reduced from 1 to $\sim$0.95. These states are LEGS. As the inset to Fig. 1 shows, their fraction, x, scales with the disorder as $x \sim (\sigma/t_0)^{2/3}$. The fraction of states exceeding the threshold C again begins to grow rapidly as C is reduced to ≤ 0.1.

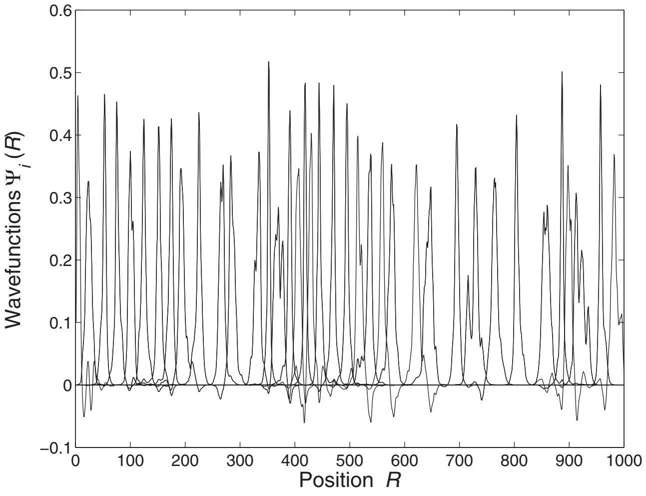

FIG. 2. The exciton center-of-mass wave functions, $\Psi_i(R)$, for the LEGS (defined by $\alpha \geq 0.95$) when $\sigma/t_0=0.1$.

Figure 2 shows the exciton center-of-mass wave functions defined for the LEGS (defined here by a signed-value parameter $\alpha \geq 0.95$). Evidently, these states are virtually nodeless, in the sense that nodes occur where the amplitude is negligible. We also note that the states are spatially localized and since they are essentially nodeless they are necessarily nonoverlapping, because of the orthogonality constraint on the wave functions. The nonoverlapping property of the wave functions is confirmed by noting that for $C=0.95$ and $\sigma/t_0=0.1$ the average spacing between the localized center-of-masses, ΔR_{COM}, is $\Delta R_{COM}=29.6$ repeat units, while the fraction of LEGS, x, is $x=0.032 \simeq \Delta R_{COM}^{-1}$.

We can show more formally that these states have the properties of locally lowest excited states by investigating the relationship between their transition dipole moment, M, and their localization length, L. The transition dipole moment of an exciton confined to a chain of N repeat units is

$$M_i = M_0 \sum_{R=1}^{N} \Psi_i(R), \tag{5}$$

where M_0 is the transition dipole moment for a single repeat unit. For the lowest-lying exciton on a *uniform* chain

$$\Psi(R) = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi R}{N+1}\right) \tag{6}$$

and therefore $M=\sqrt{8N/\pi}$ for $N \gg 1$. The localization length, L, for such an exciton, however, is

$$L = N\left(\frac{\pi^2-6}{3\pi^2}\right)^{1/2}, \tag{7}$$

and thus,

$$\left(\frac{M}{M_0}\right)^2 = \frac{8}{\pi}\left(\frac{3}{\pi^2-6}\right)^{1/2} L. \tag{8}$$

Figure 3 shows $(M/M_0)^2$ versus L for all the states calculated for a particular realization of the disorder. Clearly, the LEGS cluster around the line defined by Eq. (8) indicating

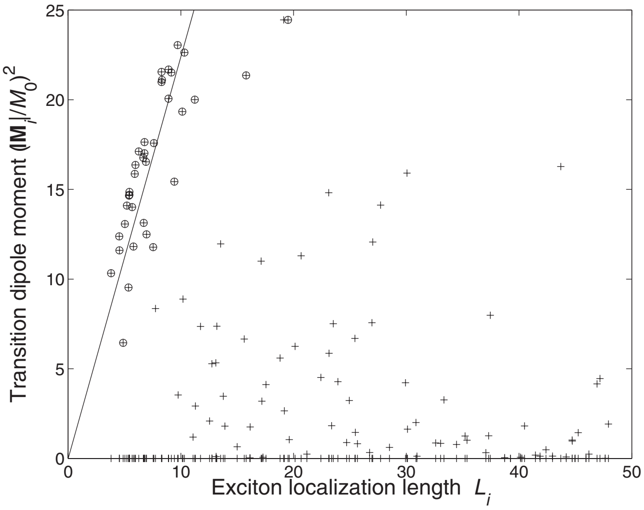

FIG. 3. The square of the dimensionless transition dipole moment versus the exciton localization length (in units of the repeat unit). The circled symbols indicate LEGS (defined by $\alpha \geq 0.95$). The line is given by Eq. (8).

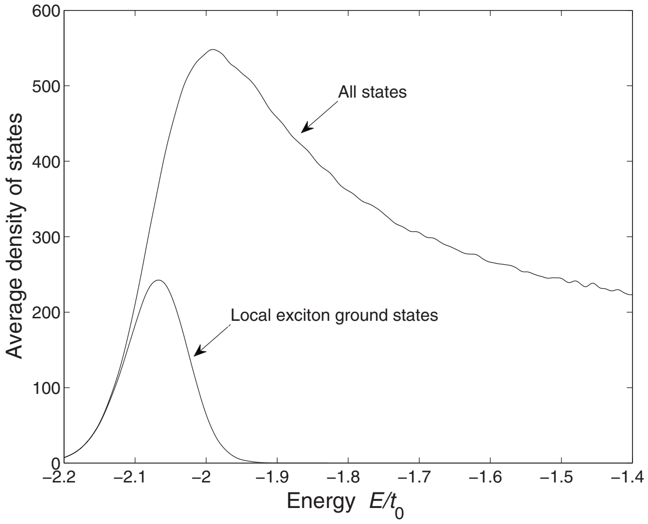

FIG. 4. The density of states averaged over 5000 realizations of the disorder, where $\sigma/t_0=0.1$. The fraction of LEGS is 3.2% for $C=0.95$. The width of the LEGS density of states $\sim\sigma^{4/3}$.

that they are indeed the locally lowest energy states. Indeed, as well as the definition that the signed-value parameter exceeds a threshold value, a LEGS can be defined as one that (within statistical fluctuations) satisfies Eq. (8).

We can now define more precisely the exciton confinement or conjugation length, ℓ: it is the nonoverlapping region of a polymer chain in which a localized exciton has a localization length, L. From Eq. (7),

$$\ell = L\left(\frac{3\pi^2}{\pi^2-6}\right)^{1/2} \simeq 2.77L. \tag{9}$$

For $C=0.95$ and $\sigma/t_0=0.1$ the ensemble averaged conjugation length is $\langle\ell\rangle=20.6$ repeat units. Bearing in mind the uncertainty in the constant of proportionality in Eq. (9), this is reasonably close to the average spacing between the localized center-of-masses ($\Delta R_{COM}=29.6$ repeat units), suggesting the LEGS define effective low-energy, nonoverlapping, and space-filling conjugated (or spectroscopic) segments.

As expected from this discussion, the ensemble average localization length of these states satisfies $\langle L\rangle \sim (\sigma/t_0)^{-2/3} \sim x^{-1}$, which is the scaling relation for localized states at the band edge.[13] Further confirmation that our threshold for the signed-value parameter α selects low-energy states is made from Fig. 4. This shows the ensemble averaged density of states of all states and of the LEGS separately, illustrating that the LEGS dominate the low-energy excitations. We also note from this figure that the density of states of the LEGS is almost normally distributed, with a width, w, scaling as $w \sim \sigma^{4/3}$, in agreement with Ref. 6 study of diagonal disorder.

In their study of the Anderson model with diagonal disorder, Malyshev and Malyshev[6] predicted local exciton "excited" states spatially localized in the region of a local exciton ground state. If such states exist in our model there should be a cluster of states in Fig. 3 around a line with a gradient nine times smaller than the LEGS line. We see no evidence for such states.[14] Since for the case of off-diagonal disorder the localization length increases with energy (up to the band center), it is clear that higher lying excited states become more extended and spatially overlapping. For $\sigma/t_0=0.1$ the largest average confinement length $\sim$140 repeat units.

We now turn to discuss the optical properties of the model. The optical absorption, $I(E)$, is defined by

$$I(E) = \left\langle \sum_i f_i \delta(E-E_i) \right\rangle, \tag{10}$$

where $\langle\cdots\rangle$ represents an ensemble average, the oscillator strength is $f_i \sim E_i M_i^2$, and M_i is defined in Eq. (5). Since the excitation energies of the LEGS are narrowly distributed at the band edge, and further since $M_i^2 \sim L_i \sim \sigma^{-2/3}$, while $x \sim \sigma^{2/3}$ we might expect that the total optical absorption from the LEGS to be independent of disorder. This is indeed confirmed by Fig. 5, which shows that the optical intensity carried by states whose value of the signed-value parameter

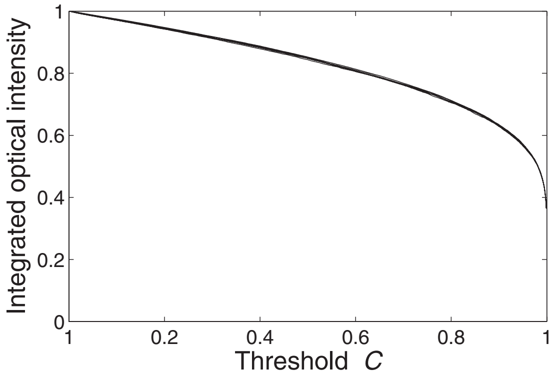

FIG. 5. The optical intensity carried by states whose signed-value parameter exceeds the threshold C. The values of σ/t_0 varies from 0.01 to 0.1. The number of repeat units, N, used was $N=1000$ and each calculation was performed over 500 realizations of the disorder.

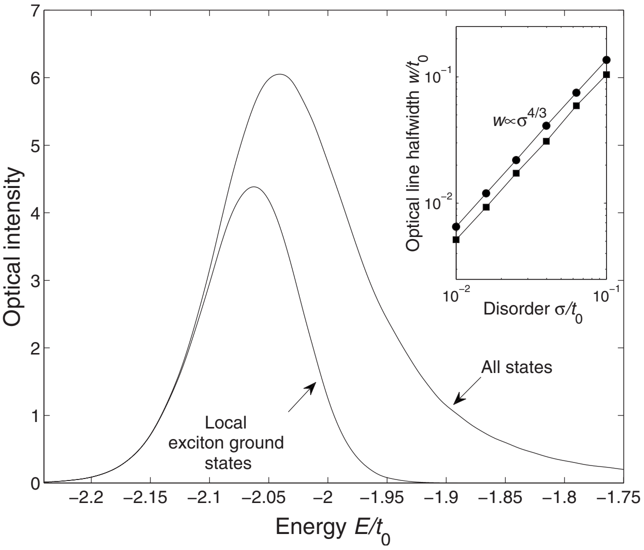

FIG. 6. The optical absorption for all the excited states and the LEGS averaged over 5000 realizations of the disorder, where $\sigma/t_0=0.1$. The LEGS contribute ~50% of the total intensity. As shown in the inset, for both cases the linewidth scales as $\sim\sigma^{4/3}$ (circles: all states; squares: LEGS).

exceeds a threshold C is essentially independent of the disorder. The total optical intensity carried by the LEGS (defined by $C=0.95$) is ~50%.

Figure 6 shows the calculated optical intensity from both the full set of states and the LEGS. The LEGS dominate the low-energy spectrum, and their mean energy is redshifted from the overall average energy by amount $\sim\sigma$. The inhomogeneous linewidth, $w\sim\sigma^{4/3}$ (in agreement with Ref. 6 and not $\sim\sigma$, as reported in Ref. 4).

We now speculate on the role of the local ground and excited exciton states on the photophysical properties of conjugated polymers. We first observe that in any region of the polymer chain the lowest energy excitation will be a local ground state. However, there will be higher lying more extended excited states that spatially overlap local exciton ground states and other excited exciton states.[4] Moreover, a local ground state may have a higher energy than a spatially separated excited state. Upon photoexcitation the ratio of local ground and excited states is approximately 1:1. It is reasonable to assume that an excited more extended state will rapidly interconvert to a spatially overlapping lower energy local ground state. This exciton can then migrate to a spatially distant local ground or to an excited state. However, since the low-energy fraction of excited states is much smaller than those of local ground states, and further since the exciton transfer integral scales as ℓ^{-1} (where the conjugation length, ℓ, is larger for excited states)[2] we may reasonably suppose that exciton migration is overwhelmingly to other local ground states. In other words, in a very short time after photoexcitation, excitons migrate through a series of spatially distinct states (or conjugated segments) whose energies are normally distributed about a mean energy whose value is lower than the mean absorption energy. This obviously implies a diffusion induced spectral red shift and quantitatively justifies the Gaussian random disorder model of exciton migration.[7]

IV. CONCLUDING REMARKS

This paper has focused on the definition and properties of LEGS in polymers with weak conformational disorder. The question now arises, how general is the concept of LEGS in polymers with different types and strengths of disorder? Malyshev and Malyshev[6] proved the existence of LEGS for weak diagonal disorder, so the combination of both weak off-diagonal and diagonal disorder should not change this description.

If, however, there are weak torsional potentials, and hence strong and probably multimodal disorder (as in P3HT, for example[5]), breaks in the π conjugation introduce the π-conjugation length, that also localizes excitons. The shorter of the π-conjugation length and the disorder-induced exciton confinement length defines the size of the low-energy spectroscopic segments. In both cases there will be LEGS that are spatially separated and nonoverlapping.

In the case of strong disorder and π conjugation breaks, however, the LEGS will not generally exhibit a Gaussian density of states. Assuming that breaks in the π-conjugation are uncorrelated, then the distribution of conjugation lengths between breaks, ℓ, follows an exponential distribution, $P(\ell)=c\exp(-c\ell)$, where c is the probability of a conjugation break per unit length. The exciton density of states is then given by $g(E)=P(\ell)d\ell/dE$, which depends on the particular definition of $E(\ell)$.

This work has neglected the role of Coulomb-induced intra- or interchain interactions. For energetically degenerate spectroscopic segments in close spatial proximity these interactions can couple the segments, delocalizing an exciton between the segments.[5] We have also neglected the role of electron-lattice coupling in further localizing excitons. This is currently under investigation.

In conclusion, LEGS are ubiquitous in disordered polymers. A LEGS is virtually nodeless and its transition dipole moment approximately satisfies Eq. (8). LEGS define the nonoverlapping and space filling low-energy spectroscopic segments. For weak Gaussian conformational disorder they are determined by the disorder-induced exciton confinement length, which scales with the disorder as $\sigma^{-2/3}$. For strong conformational disorder they are defined by breaks in the π conjugation. In general, their energetic distribution is a function of the type and strength of the disorder. For weak Gaussian disorder the optical linewidth and density of states of the LEGS scale as $\sigma^{4/3}$, and they are spectrally redshifted with respect to the rest of the states.

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APPENDIX: ACCURATE COMPUTATION OF THE DENSITY OF STATES OF THE ANDERSON MODEL

It is the purpose of this appendix to describe an efficient and accurate technique for calculating the density of states of single-particle Hamiltonians with random disorder.

The average density of states, $D(E)$, for the N-site Anderson model, Eq. (1), with a probability distribution $P(t_1,\ldots,t_{N-1})$ for $\{t\}$ is written as

$$D(E) = \int dt_1, \ldots, dt_{N-1} P(t_1,\ldots,t_{N-1}) \times \sum_k \delta(E - E_k(t_1,\ldots,t_{N-1})), \tag{A1}$$

where $E_k(t_1,\ldots,t_{N-1})$ are the eigenenergies.

A direct integration of Eq. (A1) using the Monte Carlo method results in a set of δ functions instead of a continuous spectrum. The usual approach is to replace the δ functions in Eq. (A1) by functions with a small but finite width, e.g., narrow Gaussian functions. However, this approach is very inefficient and leads to noise in the calculated spectrum (see Ref. 8). Here we apply a significantly more efficient approach that uses a transformation of the Hamiltonian parameters leading to a known transformation of its eigenenergies. Originally this approach was proposed by Makhov *et al.*[8–10] for the Anderson model with diagonal disorder, where a uniform shift of all the diagonal matrix elements of the Hamiltonian was used. For the present case of pure off-diagonal disorder, the appropriate transformation of the Hamiltonian is a uniform scaling of all of its matrix elements. Indeed, it is obvious that

$$E_k(xt_1,\ldots,xt_{N-1}) \equiv xE_k(t_1,\ldots,t_{N-1}), \tag{A2}$$

where x is a scaling parameter.

We use the scaling parameter x as an additional integration variable. Analogously to the procedure used in Refs. 9 and 10, we can rewrite Eq. (A1) as

$$D(E) = \int dt_1, \ldots, dt_{N-1} dx P(t_1,\ldots,t_{N-1}) \times \frac{x^{-N} P(t_1/x,\ldots,t_{N-1}/x)}{\int dy y^{-N} P(t_1/y,\ldots,t_{N-1}/y)} \times \sum_k \delta[E - E_k(t_1,\ldots,t_{N-1})]. \tag{A3}$$

It is easy to see that Eq. (A3) is equivalent to Eq. (A1).

Now we make the variable substitution $t_i' = t_i/x$. Taking Eq. (A2) into account, we obtain

$$D(E) = \int dt_1', \ldots, dt_{N-1}' dx \times \frac{x^{-1} P(t_1',\ldots,t_{N-1}') P(xt_1',\ldots,xt_{N-1}')}{\int dy y^{-N} P[(x/y)t_1',\ldots,(x/y)t_{N-1}']} \times \sum_k \delta(E - xE_k(t_1',\ldots,t_{N-1}')). \tag{A4}$$

Introducing the variable $z = x/y$ in the 'normalizing' integral in the denominator, Eq. (A4) now takes the form,

$$D(E) = \int dt_1', \ldots, dt_{N-1}' dx \times \frac{x^{N-2} P(t_1',\ldots,t_{N-1}') P(xt_1',\ldots,xt_{N-1}')}{\int dz z^{N-2} P(zt_1',\ldots,zt_{N-1}')} \times \sum_k \delta(E - xE_k'), \tag{A5}$$

where $E_k' \equiv E_k(t_1',\ldots,t_{N-1}')$.

Now, integrating Eq. (A5) over x, we obtain

$$D(E) = \int dt_1', \ldots, dt_{N-1}' P(t_1',\ldots,t_{N-1}') \times \sum_k \frac{\frac{E^{N-2}}{E_k'^{N-1}} P\left(E\frac{t_1'}{E_k'},\ldots,E\frac{t_{N-1}'}{E_k'}\right)}{\int dz z^{N-2} P(zt_1',\ldots,zt_{N-1}')}. \tag{A6}$$

Equation (A6) is in a very convenient form for integration with the Monte Carlo method, because the integrand has the form of a product of the initial probability distribution for $\{t\}$ and the sum of the smooth normalized functions of E.

For clarity, we omit the primes (as they are now redundant) and rewrite Eq. (A6) as

$$D(E) = \left\langle \sum_k A_k E^{N-2} P\left(E\frac{t_1}{E_k},\ldots,E\frac{t_{N-1}}{E_k}\right) \right\rangle, \tag{A7}$$

where $\langle \cdots \rangle$ represents an ensemble average over all polymers, A_k is a normalization constant for each term in the summation over k,

$$A_k = \left[\int dE E^{N-2} P\left(E\frac{t_1}{E_k},\ldots,E\frac{t_{N-1}}{E_k}\right) \right]^{-1}, \tag{A8}$$

and $E_k \equiv E_k(t_1,\ldots,t_{N-1})$.

For the case of Gaussian disorder, Eq. (A7) takes the form

$$D(E) = \left\langle \sum_k A_k E^{N-2} \exp\left(-\frac{(E-\tilde{E}_k)^2}{2\tilde{\sigma}_k^2} \right) \right\rangle, \tag{A9}$$

where

$$\tilde{E}_k = E_k \frac{t_0 \sum_i t_i}{\sum_i t_i^2}, \tag{A10}$$

and

$$\tilde{\sigma}_k = \sigma \frac{E_k}{\sqrt{\sum_i t_i^2}}. \tag{A11}$$

Since a uniform scaling of all the Hamiltonian matrix elements does not change the wave functions, the same equations can be also used to calculate the optical lineshapes for disordered polymers.

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[14] Since the Anderson model with nearest-neighbor off-diagonal disorder possess particle-hole symmetry, there is, however, a high-lying energy state spatially associated with every LEGS. In particular, for every LEGS $\Psi_i(R)$ with energy E_i there is a corresponding state $\tilde{\Psi}_i(R)=\Psi_i(R)\times(-1)^R$ with energy $\tilde{E}_i=-E_i$ (relative to an arbitrary band center).