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Disorder Effects in Dimerized Bridged Molecular Systems

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We discuss a model for transport properties in a donor−acceptor system connected by a dimerized chain. The system is assumed to be subject to site-diagonal disorder. The average spectral properties of the system are discussed by using the random matrix Wegner model (Anderson's type tight-binding Hamiltonian (TBH)) for the electronic part of the problem. In our analysis we use the "Blue's function" (functional inverse of the resolvent) formalism. For a simple one-dimensional tight-binding picture, we show that the diagonal disorder destroys the energy gap emerging as a Peierls effect in a nonperturbed system without disorder, rederiving thus the results obtained earlier using different models of site randomness.

I. Introduction

Despite their simplicity, one-dimensional systems play a crucial role in the understanding of the properties of solids, since many features of the properties of the electronic states and of the related transport properties can be discussed rigorously (see refs 1 and 2 and references therein). Current developments in molecular electronics[3] have brought the attention to the one-dimensional electronic systems as models of molecular wires.[2,3] A molecular wire is a quasi-one-dimensional molecule or ensemble of molecules that can transport charge carries between its ends. That means that a molecular wire has to be conjugated along its entire length, thus providing a series of overlapping π orbitals through which the electron delocalization is effective. It should have also a small bandgap so that the energy difference between the localized electrons and delocalized ones is small enough to make the "conduction band" easily accessible.

Quasi-one-dimensional metals and molecular wires distort spontaneously[4,5] according to the Peierls instability: the spacing between successive atoms along the chain is modulated with period $2\pi/(2k_F)$, where k_F is the Fermi wave number. The tendency toward spontaneous symmetry-breaking is particularly strong in systems with a half-filled π conductance band. The distortion leads to a pairing of successive sites along the chain, or "dimerization". The process opens an energy gap at the Fermi surface, thus lowering the energy of occupied states and stabilizing the distortion.

In the competition between the lowering of the electronic energy and the increase of the elastic energy of the polymer, the modulation of the bond length takes place. Dimerized chains can be thus described by a tight-binding Hamiltonian with alternating off-diagonal terms

$$H_{\mathrm{bridge}} = \sum_{i}^{N} \epsilon_i |\beta_i\rangle\langle\beta_i| + \sum_{i\neq j} \beta_{ij} |b_i\rangle\langle\beta_j| \qquad (1)$$

with β_{ij} being a symmetric site diagonal matrix

$$\begin{aligned} \beta_{2i,2i-1} &= \beta - t_1 \qquad \text{“single” bond} \\ \beta_{2i,2i+1} &= \beta + t_1 \qquad \text{“double” bond} \end{aligned} \qquad (2)$$

representing alternating variation between the sites. Such a Hamiltonian is relevant for polyenes and cofacially stacked polymers. For a typical example of a conjugated system of polyacetylene,[6] the dimerized structure of the chain is characterized by the π band width $4\beta = 10$ eV and the dimerization energy $2\Delta = 4t_1 \approx 1.4$ eV. Within the one-electron approximation, neglecting the effect of phonons, the above tight-binding Hamiltonian can represent also a molecular wire.[7,8] The Hückel-like models have been used in series of papers devoted to the study of the electronic response of molecular wires.[3,8] In the latter, the authors have raised the role of disorder in tight-binding wires; that is, they have studied the effect of random site energies (Hückel α parameter). Such a static diagonal disorder refers to situations when the position and nature of the groups in the wire are only known statistically. In fact, in the π-electron picture of the Hückel Hamiltonian, changing the side groups affects the energy of the site it has been attached to. For that reason, quasi-one-dimensional bridges with disorder can be models[9] of biological medium (proteins) involved in carrying the electron from donor to acceptor.

The electron density of states and localization length have been previously calculated for weakly disordered dimerized tight-binding chains (cf. refs 10−14) using various methods. In particular, it has been shown[10] that a stochastic Gaussian site disorder destroys the energy gap in the center of the band.

In what follows, we report on the effect of diagonal disorder on the localization properties of a dimerized chain that accompanies the charge transfer. Our method, based on the "free variables approach", is consistent with the CPA treatment,[15−17] as it will be briefly discussed in the next section. In section II, we review the formalism of the functional inverse of Green's function, which is used in our approach to evaluate spectral properties of the system. In sections III−V an application of Blue's function is presented; we analyze and discuss statistical properties of the TBH model with disorder, showing the effect

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of noise on the Peierls gap in a dimerized chain. In conclusion, we speculate on further applications of the formalism.

II. Disordered Chain and Random Matrix Models

Complex and disordered systems play an important role in a number of areas in physics, chemistry, and biology. The dual interplay between disorder and localization[18] and disorder and chaos[19,20] has far-reaching consequences on many aspects of modern science[21−25] at the macroscopic and microscopic levels. A neat tool used in investigating Hamiltonians of disordered systems is the random matrix theory (RMT),[21,22] where numerous calculational methods have been developed such as orthogonal polynomials, replica methods, and others. A powerful alternative to some of these methods has been the work of Voiculescu and Speicher[26,27] using the concept of "free random variables". "Free disorder" allows for exact calculations of various moments of Hamiltonians composed of random and deterministic parts. In physical systems, freeness accounts for summing over all "single-site" rescatterings, similar to the mean-field approach in many-body theory. Instead of using the standard language of Green's functions, one can choose to use their functional inverse introduced and named "Blue's functions" by Zee.[28] In many ways, the Blue's function approach is a user-friendly method providing a calculational shortcut to a more advanced approach presented in Voiculescu papers. In the former two papers,[29,30] we have used the formalism of Blue's function in the calculation of spectral properties of disordered systems. The machinery is based on the concept of additivity of Blue's functions for both Hermitian random ensembles[28] and non-Hermitian random ensembles[15,31] with arbitrary measures.

The formalism can be translated to describe spectral properties of a Hamiltonian of the form

$$H = H^{D} + H^{R} \tag{3}$$

where H^D is a deterministic and H^R a random part of the operator. By assuming that H^D and H^R are free with respect to the average over the disorder, the diagonal part of the one-particle Green function associated with the total Hamiltonian H satisfies the equation[15,17,27,28,32]

$$G(\epsilon) = G^{D}[z - \Sigma(G(z))] \tag{4}$$

where the argument of G^D is $z - \Sigma$ with Σ being nothing but the self energy determined by

$$G^{R} = \frac{1}{z - \Sigma(G^{R})} \tag{5}$$

and

$$G^{R} = \frac{1}{N}\,\mathrm{tr}\left\langle \frac{1}{z - H^{R}} \right\rangle \tag{6}$$

The same result has been rederived by Zee[28] who, through his diagrammatic analysis, introduced the "Blue's function" that is just the functional inverse of the resolvent

$$B[G(z)] = z \tag{7}$$

and satisfies the additivity law

$$B^{D+R}(z) = B^{D}(z) + B^{R}(z) \text{ - } \frac{1}{z} \tag{8}$$

Both eqs 4 and 8 coincide if one identifies $B(z) = \Sigma(z) + z^{-1}$. When the averaging in eq 6 is done over the ensemble of $N \times N$ random Hermitian matrices generated with the Gaussian probability

$$P(H) = \frac{1}{Z}\, \mathrm{e}^{-N \mathrm{tr} H^{2}/(2\sigma^{2})} \tag{9}$$

standard calculations[21] give

$$G^{R}(z) = \frac{1}{2\sigma^{2}}\left(z - \sqrt{z^{2} - 4\sigma^{2}}\right) \tag{10}$$

which together with the eq 7 lead to Blue's function

$$B^{R}(z) = \sigma^{2} z + \frac{1}{z} \tag{11}$$

The property in eq 8 bears much in common with the CPA treatment[16,17] of the Hamiltonian eq 3 for which the H_R part is the diagonal random matrix with random entries V. The CPA method requires[4]

$$\left\langle \frac{V - \Sigma}{1 - (V - \Sigma)G} \right\rangle = 0 \tag{12}$$

with Green's function fulfilling the condition of eq 4. By multiplying by $G(z)$ and adding and substracting 1 in the numerator, the above formula reads[6]

$$G(z) = \left\langle \frac{1}{G^{-1} + \Sigma - V} \right\rangle = G_{R}(G^{-1} + \Sigma) \tag{13}$$

By taking the functional inverse (Blue's function) of the random part of $G(z)$ in eq 13 and the deterministic part of $G(z)$ in eq 4 one obtains

$$B_{R}(G) = \frac{1}{G} + \Sigma$$

After the substitution $z = B(G(z))$, the sum of B_R and B_D can

$$B_{D}(G) = z - \Sigma \tag{14}$$

be reexpressed in terms of eq 8, bringing the argument about the CPA character[16,17] of the method.

III. Spectral Density and Conductance

A molecular wire can be understood as a connecting unit that is able to transfer electrons between two components.[2,3] Important applications of molecular wires range from molecular electronics[7,33] to bridge-mediated electron transfer[8,9,30,34−36] in biological systems, where the transfer of electron proceeds from donor to acceptor through a bridge connecting them. The ability to transfer charges between terminal points of the wire is measured in terms of conductance, which at low temperature (and in the dc limit, $\omega \to 0$) can be expressed in terms of the spectral function via the Kubo−Greenwood relation[4,37]

$$g_{T=0}(\omega) = \mathrm{const}\, \frac{2e^{2}}{\pi V_{B}}\, \nu^{2}(\epsilon{=}E_{F}) \tag{15}$$

where E_F stands for the Fermi energy, e is a unit charge, V_B represents the volume of the first Brillouin zone, and $\nu(\epsilon)$ is the density of electronic states in the wire. By changing to a complex variable, the density of eigenvalues can be conveniently defined in terms of the trace of the resolvent of the wire (bridge) Hamiltonian

$$G(\epsilon) = \frac{1}{N}\,\mathrm{tr}\left\langle \frac{1}{\epsilon - H_{\mathrm{bridge}}} \right\rangle \tag{16}$$

The density of states for H_{bridge} is then given by

$$\nu(\epsilon) = \frac{1}{N}\,\mathrm{tr}\,\langle \delta(\epsilon - H_{\mathrm{bridge}}) \rangle = -\frac{1}{\pi}\,\mathrm{Im}G(\epsilon + i\lambda) \tag{17}$$

in the limit of $\lambda \to 0$ and follows from the discontinuities of the resolvent (eq 16) along the ϵ-axis. In the Peierls theory the one-domensional bridge Hamiltonian is of the form

$$H_{\mathrm{b}} = \begin{pmatrix} 0 & \beta + t_1 & & \\ \beta + t_1 & 0 & \beta - t_1 & \\ & \beta - t_1 & 0 & \beta + t_1 \\ & & \text{etc.} & \end{pmatrix} \tag{18}$$

with alternating coupling strengths and $t_1 = \Delta/2$. The deterministic resolvent of such a model $N \times N$ Hamiltonian, in the limit of large N, is[6]

$$G^{\mathrm{D}}(\epsilon) = \frac{\pm i\epsilon}{\sqrt{(\epsilon^2 - 4\beta^2)(\Delta^2 - \epsilon^2)}} \tag{19}$$

Blue's function, the function inverse of the resolvent, may be found easily,

$$(B^{\mathrm{D}}(\epsilon))^2 = \frac{1}{2}[4\beta^2 + \Delta^2 + 1/\epsilon^2 \pm \sqrt{(4\beta^2 + \Delta^2 + 1/\epsilon^2)^2 - 16\beta^2\Delta^2}] \tag{20}$$

As it stands, the bridge TBH Hamiltonian, eq 18, can be generalized, as in the case of the Anderson model, to include disorder of the bridge chain. In what follows, we will adopt the model of the site diagonal disorder that is equivalent to the ones studied by Wegner[37] and Neu and Speicher.[17,27] The idea of Wegner was to generalize the Anderson model by putting n electronic states at each site of the d-dimensional lattice and describing the disorder by Gaussian random matrices in the electronic states. For $n = 1$ Wegner's model reduces to the usual unsolvable Anderson model and becomes exactly solvable for $n \to \infty$. Adding a Gaussian noise to the (deterministic) bridge, with Blue's function $B^{\mathrm{R}}(\epsilon) = \sigma^2\epsilon + 1/\epsilon$ yields Blue's function of the deterministic plus random system given by eq 8. By inverting the resulting expression, one finds a sixth-order equation to the resolvent of the full system,

$$(\epsilon - \sigma^2 G)^4 - (\epsilon - \sigma^2 G)^2\left(4\beta^2 + \Delta^2 + \frac{1}{G^2}\right) + 4\beta^2\,\Delta^2 = 0 \tag{21}$$

At $\epsilon = 0$ this can be reduced to a second-order equation

$$G^2(\epsilon = 0) = \frac{4b^2 + \Delta^2 - \sqrt{(4\beta^2 - \Delta^2)^2 + 4\sigma^4}}{2\sigma^4} \tag{22}$$

For small noise, σ, the resolvent is real, reaching zero at ${\sigma_c}^2 = 2\beta\Delta$, and for $\sigma > \sigma_c$ the resolvent is imaginary, indicating a nonvanishing spectral density. Thus, for a critical value of the noise intensity σ_c we observe the disappearance of the energy gap induced by the Peierls instability; 2Δ shrinks to zero. Indeed, this is shown in Figure 1 for a specific choice of β and Δ parameters.

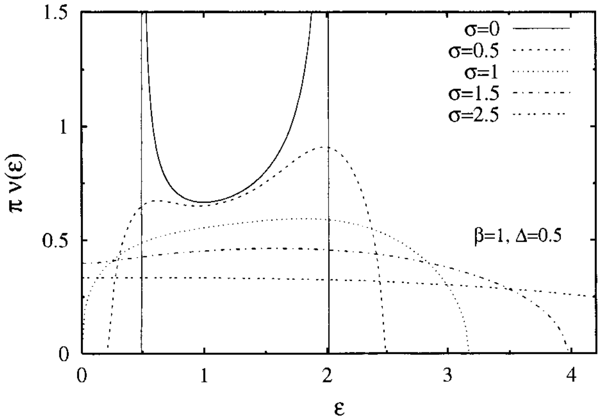

Figure 1. Spectral density of the Peierls bridge with $\beta = 1$, $\Delta = 0.5$, and varying noise strengths σ for nonnegative energies. Note that by eq 21, the spectral density in this case is symmetric in energies ϵ.

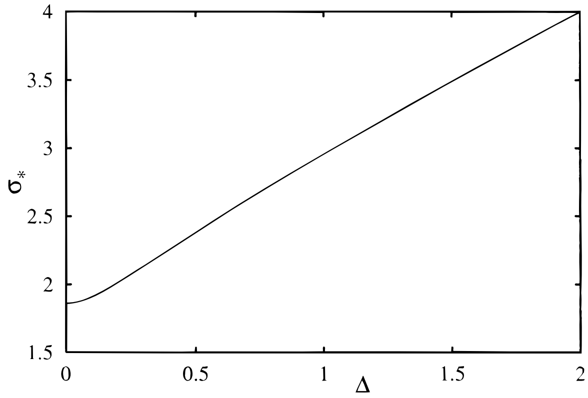

Figure 2. Critical strength σ_* in rescaled units ($\Delta \to \Delta/\beta$, $\sigma \to \sigma/\beta$).

The "deterministic" spectrum is divergent close to the endpoints of the bands (-2β, $-\Delta$) and (Δ, 2β), reproducing the results of former analysis.[14,10] For an increasing value of the noise intensity σ, the distribution $\nu(\epsilon)$ flattens and the Peierls gap disappears. Eventually, the spectral density changes from the four-modal function with two peaks located at the ends of the positive (negative) support to the unimodal distribution with a broad hump around the center of the support. Similar conclusions have been drawn in ref 10 using, however, a different method of calculating averages over the randomized site energies.

The change from the four-modal to unimodal distribution of eigenenergies is characterized by a vanishing second derivative of the resolvent around the center of the band, $\epsilon = 0$. Expanding eq 21 around $\epsilon = 0$ up to the second order, the critical noise strength σ_* is given by the third-order equation ($\beta = 1$)

$$4({\sigma_*}^4)^3 - [3(\Delta^2 - 4)^2 + 256\Delta^2]\,({\sigma_*}^4)^2 - 192\Delta^2\,(\Delta^2 - 4)^2{\sigma_*}^4 - 36\Delta^2\,(\Delta^2 - 4)^4 = 0 \tag{23}$$

The general solution may be expressed analytically, however lengthy. For a small gap ($\Delta < 0.1$), we find

$${\sigma_*}^4 \approx 12\left(1 + \frac{23}{2}\Delta^2\right) \tag{24}$$

with ${\sigma_*}^4 = 12$ for the gapless case. For the demonstrated choice $\Delta = 0.5$ we found $\sigma_* = 2.38$, and in the limiting case $\Delta \to 2$, $\sigma_* \to 4$ (see Figure 2). From the above considerations, we can deduce that the dc conductivity at zero temperature, which is given by the square of the spectral function (cf. eq 15) depends essentially on the strength of the noise. Above the critical value of the noise intensity, $\sigma_c^2 = 2\beta\Delta$, the conductivity becomes nonvanishing everywhere inside the band.

IV. Localization Constant

Transport properties of the model system can be also described in terms of the localization constant.[1,4,5,38] For the inverse localization length $\gamma \equiv 1/l$, the localization constant is defined as

$$\gamma = -\lim_{N\to\infty}\frac{1}{N}\ln|G_{1,N}| \tag{25}$$

On the other hand, $t(N,\epsilon) = |G_{1N}(\epsilon)|^2$; i.e., the square of the matrix element of $G(\epsilon)$ between the states that correspond to the first and the Nth sites of the connector gives the transmission probability for a particle to be transferred from site 1 to site N.

The matrix element $G_{1,N}$ of the full (deterministic plus random) system once again may be related to the same element of the deterministic system[16,27,30]

$$G_{1N}(\epsilon) = G_{1N}^{\mathrm{D}}(\epsilon - \Sigma[G(\epsilon)]) \tag{26}$$

with the self energy of the random interaction, $\Sigma[G] = \sigma^2 G$. The deterministic matrix element is easy to evaluate:

$$\begin{aligned} G_{1N}^{\mathrm{D}} &= \frac{-(\beta+\Delta/2)^{N/2-1}(\beta-\Delta/2)^{N/2}}{\det H_{\mathrm{b}}} && N \text{ even} \\ &= \frac{(\beta^2-\Delta^2/4)^{(N-1)/2}}{\det H_{\mathrm{b}}} && N \text{ odd} \end{aligned} \tag{27}$$

The determinant $\det(\epsilon) = \det H_{\mathrm{b}}$ can be evaluated knowing the resolvent (eq 19) by integration, since

$$G(\epsilon) = \partial_\epsilon F(\epsilon) \tag{28}$$

where $Z = \langle \det(\epsilon)\rangle$ can be interpreted as a partition function

$$F(\epsilon) = \frac{1}{N}\log\langle\det(\epsilon)\rangle$$

with $F(\epsilon)$ being a free energy analogue.[16] Direct integration yields

$$\det(\epsilon) = \left(\frac{\sqrt{\epsilon^2-\Delta^2} \pm \sqrt{\epsilon^2-4\beta^2}}{2}\right)^N \tag{29}$$

with the asymptotic $\det(\epsilon) \to \epsilon^N$ for large ϵ. Dropping the subleading ($O(1/N)$) terms, the "deterministic" localization constant is

$$\gamma_{\mathrm{D}}(\epsilon) = \log\frac{\sqrt{\epsilon^2-4\beta^2} + \sqrt{\epsilon^2-\Delta^2}}{\sqrt{4\beta^2-\Delta^2}} \tag{30}$$

in the case of the bridge alone. For the full system (with noise included) we make use of eq 26:

$$\gamma(\epsilon) = \gamma_{\mathrm{D}}[\epsilon - \sigma^2 G(\epsilon)] \tag{31}$$

In the $\Delta \to 0$ limit these formulas reduce to the ones discussed in the previous work.[30]

There is an interesting numerical observation: for small gaps the most stable states are the ones around $\epsilon = 1$ (in units of β) with infinite localization length. However, even the smallest noise yields a nonzero value of γ at that point. After disappearance of the Peierls gap, for noise intensities bigger than $(2\beta\Delta)^{1/2}$ the most stable states have energies around the point $\epsilon = 0$.

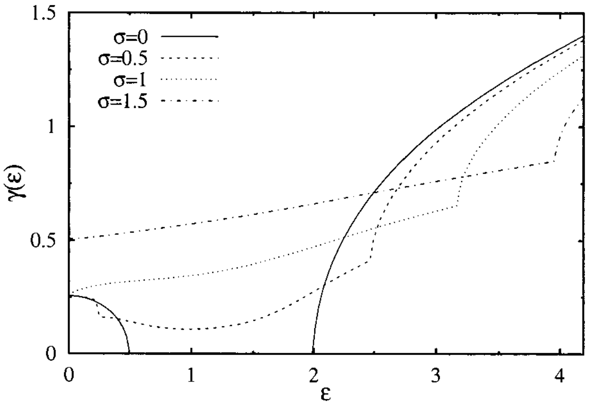

Figure 3. Localization constant as the function of the energy with $\beta = 1$, $\Delta = 0.5$, and varying noise strengths σ.

V. Model of a Molecular Wire

So far, in our discussion we have omitted the effect of terminal components (electrodes; donor and acceptor units) that are connected by a molecular wire. A more general description would require considering a system composed of two noninteracting reservoirs of electronic states to which the molecular chain is attached. The interaction between the electrodes and the wire can be incorporated into the effective transfer matrix element through Green's function of the total "wire plus reservoirs" Hamiltonian. Within the Newns−Anderson chemisorption model,[7,8] assuming half-filling, and for the transfer between identical electrodes, the effect of reservoirs can be lumped into the site energies ϵ_1 ..., ϵ_N through the chemisorption coupling. Formally, it leads to substitution[7]

$$\begin{aligned} \epsilon_1 &\to \epsilon_1 + i\Lambda_1 \\ \epsilon_N &\to \epsilon_N + i\Lambda_N \end{aligned} \tag{32}$$

where Λ stands for the chemisorption coupling.

In the deterministic case and for a finite homogeneous bridge of N units the $G_{1,N}$ element reads[7,8]

$$G_{1,N} = \frac{(-1)^{N-1}\prod_{i=1}^{N-1}\beta_{i,i+1}}{d_N - 2d_{N-1}\Sigma_1 + d_{N-2}\Sigma_1\Sigma_N} \tag{33}$$

where d_N is a determinant of the tridiagonal $N \times N$ matrix, $d_N = \det(\epsilon - H_{\mathrm{b}})$, and $\Sigma_1 = \Sigma_N$ are self energy corrections both set up to $i\Lambda$. Note that in the large N limit, this formula is essentially the same as for the case of a pure molecular wire with no electrodes attached. The only difference is a multiplicative factor $(1 + i\Lambda)^{-2}$. Given the effective Hamiltonian, the small voltage, low-temperature conductance of the wire is[7]

$$g = \frac{2e^2}{\hbar\pi}\Delta^2|G_{1,N}(0)|^2 \tag{34}$$

and can be analyzed within the formalism of section IV. Again, using eqs 4 and 26 or eq 8 would be equivalent to the coherent potential approximation (CPA limit).[16,17] The "free random variables" approach is also relevant for non-Gaussian statistics. That renders the Blue's function formalism as a beneficial method because of its appealing simplicity.

VI. Conclusions

The main objective of this contribution was to present an efficient tool to study spectral properties of disordered systems. The method has been previously introduced in a series of papers[15,28,31] and succesfully applied in various models of dissipation[29] and transport in disordered media.[30] As mentioned above, the transport properties of the system are influenced by the localization properties of the electronic states. The model studied in the paper refers to the situation when the bridge (or a wire) is long enough to be considered infinite. We have analyzed an array of elements with the alternating coupling between the bridging orbitals along the chain. Owing to the Peierls effect,[5] a one-dimensional lattice with an equal overlapping integral between the nearest-neighboring sites stabilizes through a dimerization process that effectively leads to an alternate bond length structure. A perfectly dimerized chain can be described by a Hückel-type Hamiltonian (eq 1). In a dimerized chain a gap band of width 2Δ is formed. In the paper, site diagonal disorder is assumed to be in the form of a random matrix model, resulting in placing at each site of the bridging chain a random matrix with a semicircular distribution of energies (Wegner model[37]). That would correspond to a situation where the bridge energies are *n*-electron functions.

The site diagonal disorder imposed on the TBH Hamiltonian can reduce, and eventually destroy, the Peierls gap, the effect of which has been reported in literature previously (cf. ref 10 and references therein). The presence of noise extends and flattens the spectrum of the TBH Hamiltonian, leading to a one-interval energy support for values of noise intensity bigger than the critical $\sigma_c = (2\beta\Delta)^{1/2}$. If noise intensities exceed that value, dc conductivity becomes finite everywhere inside the band. For ϵ, the energy splitting between the Fermi level and the site energies sampled from the center of the TBH band, the noise increases the inverse localization length γ and leads to a fast decay of the electronic coupling $|G_{1,N}(\epsilon)|^2$ with the distance measured in chain units. That would reduce the electronic part of the kinetic rate for charge-transfer processes along the chain.

The random matrix techniques in the Blue's function formalism can be also applied to non-Hermitian Hamiltonians.[15,16,31] This approximation is then identical[16] with the conventional CPA approximation used in the theory of disordered systems.[4] The models of non-Hermitian Hamiltonians offer a new field of investigation[38] not only in the theory of quantum dissipative systems[24,31,29] but also in a variety of models with directed diffusion, such as models for the growth of bacterial populations, diffusion−reaction models of chemical reaction, or models of spreading of genetic mutations. We believe that the simplicity of the Blue's function formalism makes it worth pursuing in studies of this vast family of problems in biological and chemical applications.

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