Bridged-assisted electron transfer. Random matrix theory approach.

Ewa GUDOWSKA-NOWAK 1,3 Gábor PAPP 2 and Jürgen BRICKMANN 1
1 Institute for Physical Chemistry Technische Universität Darmstadt, Petersenstr. 20, D-64287, Germany;
2 GSI, Plankstr. 1, D-64291 Darmstadt, Germany & Institute for Theoretical Physics, Eötvös University, H-1088 Budapest, Hungary;
3 Institute of Physics, Jagiellonian University, 30-059 Kraków, Poland.

(October 24, 2018)

We discuss the effective donor/acceptor coupling for a bridged electron transfer system with a site-diagonal disorder of bridge energies. The average spectral properties of the system are discussed by using the Wegner model (Anderson’s type tight-binding Hamiltonian (TBH)) for the electronic part of the problem. Spectral properties of the system are discussed using the concept of the functional inverse of the resolvent (“Blue’s function”, [2]) for various limits of noise versus site-coupling ratio.

I. INTRODUCTION

Electron transfer (ET) processes play a fundamental role in chemistry [3] and biology [4] with the range of their abundance ranging from photosynthesis and oxidative phosphorylation to molecular electronic design. In numerous biological examples of ET reaction, a single electron is tunneling in an inhomogeneous medium over large distances of several angstroms. The intervening medium can be either a protein backbone or a sequence of cofactors embedded in a protein matrix. Due to a large separation between the donor and acceptor, direct electronic coupling between the chromophores is negligible, rendering thus the question on the effect of medium on enhancement of the electronic coupling [4]. The typical suggestion is that the ET is mediated through the bridge and influence the kinetic ET rate. Our studies of the bridge Hamiltonian are further estimated in the large number of bridge orbitals. For such an extended system, we study effect of the noise on density of bridge electronic states. The analysis is performed within the framework of the random-matrix theory [7] which turned out to be quite general and a powerful phenomenological approach to a description of various phenomena such as quantum chaos [11], complex nuclei [12], chaotic scattering [13] and mesoscopic physics [14]. Aspects of vastly different physical situations such as electron localization phenomena in disordered conductors and semiconductors [15], disordered quantum wires [16] and quantum Hall effect [17] can be described in the language of the random matrix theory. In all the realms mentioned above, the Hamiltonian of the system is rather intricate to be handled or simply unknown. In such cases the integration of the exact equations is replaced by the study of the joint distribution function of the matrix elements of the Hamiltonian $P(\mathbf{H})$.

The natural way of addressing the problems of randomness coupled to various sources is to use technique of the “free random variables” [18–21]. This method provides an elegant way of “linearizing” the process of determining the average eigenvalue distributions for convolutions representing an analogue of the logarithm of Fourier transformation of the usual convolutions. Recently, the generalization of the “addition law” for hermitean random matrices to the non-hermitean case has been derived [21] and applied by us [22] to study properties of a dissipative two-level system. Similar diagrammatic approach has been used by other authors [23] to investigate spectral properties of the Fokker-Planck operator that describes particles diffusing in a quenched random velocity field.

The paper is organized as follows. In Sections 2 and 3 we discuss briefly the model Hamiltonian reporting results known from the literature. Spectral properties of the bridge Hamiltonian are further estimated in the large $N$ limit. In Section 4 a model of disorder superimposed on a tight binding Hamiltonian of Sec.2 is presented. By use of the concept of “free variables”, we estimate Green function of the disordered system. Average properties of the system can be further inferred by studying the structure of the distribution of eigenvalues of the bridge Hamiltonian which follows derivation of the Green function for...
the model.

II. PARTITIONING TECHNIQUE, EFFECTIVE COUPLING AND GREEN FUNCTION OF THE BRIDGE.

The transferring system is assumed to have an electronic part described by a tight-binding (Hückel) Hamiltonian

\[ H = \epsilon(|D\rangle\langle D| + |A\rangle\langle A|) + H_{\text{coup}} + H_{\text{bridge}} \]  

(2.1)

where \( \epsilon \) stands for the energy of both donor and acceptor states \(|D\rangle, |A\rangle\) (for simplicity they are taken here to be equal) and the coupling \( H_{\text{coup}} \) and bridge \( H_{\text{bridge}} \) Hamiltonians are given by

\[ H_{\text{coup}} = \sum_i N \left( \beta_D |D\rangle\langle b_i| + \beta_A |A\rangle\langle b_i| \right) + hc \]  

(2.2)

and

\[ H_{\text{bridge}} = \sum_i N \epsilon_i |b_i\rangle\langle b_i| + \sum_{i\neq j} \beta_{ij} |b_i\rangle\langle b_j| \]  

(2.3)

with \( \beta_{ij} \) being a symmetric site-diagonal matrix.

The effective Hamiltonian is obtained by the standard Wigner–Weisskopf reduction [7,26,27] by partition. In this method the total Hilbert space of the problem is divided into two subspaces (spanned by donor and acceptor states and bridge states, respectively) and the Hamiltonian is integrated over the elements of one of them (here, the bridge states), eventually mapping the eigenvalue problem of a high dimension onto a lower one. The time-independent Schrödinger equation for the partition scheme is

\[ (H - E I)c = M c = 0 \]  

(2.4)

with matrix \( M \) given by

\[ M = \begin{pmatrix} M_{aa} & M_{ab} \\ M_{ba} & M_{bb} \end{pmatrix} \]  

(2.5)

By eliminating subspace “b” (spanned by intervening bridge states \(|b_i\rangle\)), the effective Schrödinger equation becomes

\[ (M_{aa} - M_{ab}M^{-1}_{bb}M_{ba})c_a = \tilde{M}_{aa}c_a = 0 \]  

(2.6)

so that the reduced effective Hamiltonian of the system is the \( 2 \times 2 \) matrix

\[ H_{\text{eff}} = \tilde{M}_{aa} + EI_a \]  

(2.7)

with energy \( E \) set up (in zeroth order) to \( \epsilon \), i.e. to donor/acceptor energy. The formalism yields the effective coupling given by [8,25]

\[ H_{DA} = -\sum_i \beta_{Di}[M^{-1}_{bb}]_{ij}\beta_{jA} \]  

(2.8)

where bracketed expression stands for the Green function of the bridge

\[ G(\epsilon) = (H_{\text{bridge}} - \epsilon)^{-1} = M^{-1}_{bb} \]  

(2.9)

with \( H_{\text{bridge}} \) given by the TBM,

\[ H_{\text{bridge}}^{mn} = \epsilon_b\delta_{mn} + \beta(\delta_{m,n+1} + \delta_{m,n-1}) \]  

(2.10)

The Hamiltonian above describes a system with \( N \) localized sites, each with energy \( \epsilon_b \) and a hopping between the neighboring sites with hopping parameter \( \beta \).

From the spectral representation of the Green’s function (2.9)

\[ G_{mn} \equiv \sum_i \frac{u^*_{im}u^*_{jm}}{\epsilon - \epsilon_i} \]  

(2.11)

with eigenvalues

\[ \epsilon_i = \epsilon_b + 2\beta \cos(\frac{\pi i}{N + 1}) \]  

(2.12)

and spectral coefficients

\[ u^*_{im} = \left(\frac{2}{N + 1}\right)^{1/2} \sin(\frac{\pi mi}{N + 1}) \]  

(2.13)

it follows, that

\[ TrG(\lambda) = \frac{1}{N} \sum_i \frac{1}{\lambda - \epsilon_i} - \int d\epsilon \frac{\nu(\epsilon)}{\lambda - \epsilon} \]  

(2.14)

where in the limit of \( N \to \infty \) we have replaced the sum in (2.9) by an integral with the level density \( \nu(\epsilon) \) as a weight. The localization length \( \gamma^{-1} \) measuring the decay of an eigenvector over the chain composed of \( N \) units can be deduced from eq.(2.11) [28]

\[ \gamma = \frac{1}{N} \sum_{\mu \neq \nu} \log |\nu_{\mu} - \nu_{\nu}| \]  

(2.15)

and in the limit of an infinite chain reads

\[ \gamma(\epsilon) = \int d\epsilon \nu(\epsilon) \log |\epsilon_{\nu} - \epsilon| - \log \beta \]  

(2.16)

bringing the dependence on the density \( \nu(\epsilon) \).

By changing to complex variable, the density of eigenvalues can be conveniently defined in terms of the trace of the resolvent of the Hamiltonian

\[ G(\epsilon) = \frac{1}{N} \text{Tr} \left\{ \frac{1}{\epsilon - H_{\text{bridge}}} \right\} \]  

(2.17)

The density of states for \( H_{\text{bridge}} \) is then given by

\[ \nu(\epsilon) = \frac{1}{N} \text{Tr} \left\{ \delta(\epsilon - H_{\text{bridge}}) \right\} = -\frac{1}{\pi} \text{Im}G(\epsilon + i\lambda) \]  

(2.18)

and follows from the discontinuities of the resolvent (2.17) along the \( \epsilon \)-axis.
III. KINETIC RATE.

The kinetic rate for the electron transfer mediated by the bridge can be evaluated according to the definition

$$k(t) = \frac{d}{dt} |\langle \phi_f | \psi_i(t) \rangle|^2$$

(3.19)

where $|\phi_f\rangle$ is a final state and

$$\psi_i(t) = e^{\frac{-i\pi H_0 t}{\hbar}} e^{-\frac{i\lambda}{\hbar} t} \psi_i$$

(3.20)

with $\psi_i$ standing for the exact eigenstate of the Hamiltonian (2.1). The latter can be decomposed into $H = H_0 + H_1$ in which $H_0$ describes diagonal part of the total Hamiltonian and $H_1$ defines interaction inducing charge transfer between the donor and acceptor [8]. The exact eigenstates of $H$ can be represented as

$$\psi_i = \phi_i + \frac{1}{\epsilon_i - H_0 + i\lambda} H_1 \psi_i$$

(3.21)

where $\phi_i$ is the initial state of the system and

$$T = H_1 + H_1 \frac{1}{\epsilon_i - H_0 + i\lambda} H_1$$

(3.22)

stands for the transition operator which to the lowest order of approximation is given by

$$T = H_1 + H_1 \frac{1}{\epsilon_i - H_0 + i\lambda} H_1$$

(3.23)

By use of the transition operator, the kinetic rate (3.19) can be rephrased in the form

$$k = \frac{2\pi}{h} |\langle \phi_f \rangle T |\phi_i\rangle|^2 \delta(\epsilon_f - \epsilon_i)$$

$$= \frac{2\pi}{h} |\langle \phi_f | H_1 | \psi_i \rangle|^2 \delta(\epsilon_f - \epsilon_i).$$

(3.24)

By assuming that the vibrational relaxation in the molecular system is much faster than the electron transfer, the above equation can be expressed as

$$k = \frac{2\pi}{h} \sum_{v,v'} \sum_{v'} P_{iv} \langle \psi_{fv'} | T | \psi_{iv'} \rangle^2 \delta(\epsilon_{fv'} - \epsilon_{iv})$$

(3.25)

where (if) and (v, v') stand for electronic and vibronic states, respectively and $P_{iv}$ is Boltzmann weight factor. In the adiabatic approximation, the wavefunctions of the system can be written as products of electronic and vibronic wavefunctions

$$\psi_{iv} = \Phi_i \Theta_{iv}.$$ 

(3.26)

Substitution of the above approximation to the evaluation of matrix elements of $T$ yields

$$\langle \psi_{fv'} | T | \psi_{iv} \rangle = \langle \Phi_{fv'} | H_{1fi} | \Theta_{iv} \rangle$$

$$+ \sum_{m,v'} (\langle \Theta_{fv'} | H_{1fm} | \Theta_{mv} \rangle (\langle \Theta_{mv} | V_{mi} | \Theta_{iv} \rangle)$$

(3.27)

In the above formula, elements $H_{1fm}$ represent electronic matrix elements between states $\Phi_f$ and $\Phi_m$. Condon approximation [3,4] allows for factorization of these terms from the Franck-Condon factors $\langle \Theta_{fv'} | \Theta_{iv} \rangle$, and in the case when the electronic gap between the donor and acceptor states is larger than vibrational energies in the system, leads to the ET rate

$$k = \frac{2\pi}{h} |T_{fi}|^2 \sum_{v,v'} P_{iv} |\langle \phi_f | \psi_{iv} \rangle|^2 \delta(\epsilon_{fv'} - \epsilon_{iv}).$$

(3.28)

The rate constant can be thus written as a product of electronic part and nuclear part, averaged over vibrational states. Throughout the paper we will focus on electronic degrees of freedom and estimation of the transition matrix (3.27).

Note, that by neglecting a direct electronic coupling between the donor and acceptor and interpreting

$$\langle \Phi_f | H_1 | \Phi_N \rangle = \langle \phi_f | H_1 | \phi_i \rangle = \beta_1$$

(3.29)

the formula for the transition matrix (3.27) is identical with the the effective coupling (2.8) and for the chain of $N$ elements of the bridge reduces to [8]

$$T_{fi} = H_{DA} = (-1)^N \frac{\beta_1^2 \beta N^{-1}}{(\epsilon_b - \epsilon)^N} = -\beta^2 G_{1N}$$

(3.30)

where the element $G_{1N}$ of the Green’s function is

$$G_{1N} = \frac{(-1)^{N+1} \beta N^{-1}}{det H_{bridge}}$$

(3.31)

with $det$ standing for the determinant of the bridge Hamiltonian (2.10).

$$det_N = \frac{\beta^N [\alpha + \sqrt{\alpha^2 - 1}]^{N+1} - (\alpha - \sqrt{\alpha^2 - 1})^N}{2\sqrt{\alpha^2 - 1}}$$

(3.32)

with

$$\alpha = \frac{\epsilon - \epsilon_b}{2\beta}.$$

(3.33)

In the $N \rightarrow \infty$ limit $det$ approaches $\beta^N$ for $|\alpha| < 1$ and $\infty$ otherwise, thus the transfer element $G_{1N}$ is $1/\beta$ for a small donor-bridge energy splitting ($|\alpha| < 1$), and 0 for tunneling energies outside the band of the width $2\beta$ (the latter corresponds to the Bloch-like extended states of the bridge [8]).

Localization constant introduced in the former paragraph is related to the decay of the transfer matrix [28]

$$\gamma = - \lim_{N \rightarrow \infty} \frac{1}{N} \ln |G_{1N}|$$

(3.34)
and, in the case of disordered bridge, would require using the density function \( \nu(\epsilon) \) to estimate the average (2.16).
In the deterministic case (no site diagonal ‘disorder’) one has
\[
\gamma = \begin{cases} 
0 & \text{if } |\alpha| < 1 \\
\text{max log} |\alpha \pm \sqrt{\alpha^2 - 1}| & \text{if } |\alpha| > 1 
\end{cases}.
\] (3.35)
so that the states with energies lying within the band \((-2\beta, 2\beta)\) are localized over the infinite range.

IV. TRANSITION THROUGH THE DISORDERED CHAIN. RANDOM MATRIX MODELS.

As it stands, the bridge Hamiltonian (tight-binding Hamiltonian TBH, eq. (2.3)), 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 which is equivalent to the ones studied by Wegner [29] and Neu and Speicher [13, 28]. 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 \( n \to \infty \).

Further generalization of Wegner’s model has been discussed by Neu and Speicher who have used a mathematical concept of “freeness” to use a more general ensembles of random matrices allowing arbitrarily distributed disorder. “Freeness”, introduced in mathematical literature by Voiculescu, Pastur and Speicher [18, 19, 22] has been also popularized recently in physical applications by Brezin, Zee, Janik et al. [2, 20, 21].

The formalism can be translated to describe spectral properties of a Hamiltonian of the form
\[
H = H^D + H^R
\] (4.36)
where \( H^D \) is deterministic, and \( H^R \) random part of the operator. By assuming that \( H^D \) and \( H^R \) are free with respect to average over the disorder, Voiculescu, Pastur, Neu and Speicher have shown that the diagonal part of the one-particle Green function associated with the total Hamiltonian \( H \) satisfies equation
\[
G(\epsilon) = G^D(\epsilon - \Sigma(G(\epsilon)))
\] (4.37)
where the argument of \( G^D \) is \( \epsilon - \Sigma \) with \( \Sigma \) being nothing but the self energy determined by

\[
G^R = \frac{1}{\epsilon - \Sigma(G^R)}
\] (4.38)
where
\[
G^R = \frac{1}{N} \text{Tr} \left\{ \frac{1}{\epsilon - H^R} \right\}. \quad (4.39)
\]
The same result has been redervied by Zee [3] who through his diagrammatic analysis, introduced the "Blue’s function" that is just the functional inverse of the resolvent
\[
B[G(\epsilon)] = \epsilon
\] (4.40)
and satisfies the additivity law
\[
B^{D+R}(\epsilon) = B^D(\epsilon) + B^R(\epsilon) - \frac{1}{\epsilon}.
\] (4.41)

Both equations (4.37) and (4.41) coincide if one identifies \( B(\epsilon) = \Sigma(\epsilon) + \epsilon \).

Our further analysis is based on the assumption that nodal energies of the bridge are randomly distributed with off-diagonal elements of matrix \( H_{\text{bridge}} \) being constant. In the limit of large \( N \), deterministic resolvent of the bridge Hamiltonian yields
\[
G^D(\epsilon) = \frac{1}{N} \sum_{k=1}^{N} \frac{1}{\epsilon - 2\beta \cos \frac{\pi k}{N+1}}
\] (4.42)
\[
\lim_{N \to \infty} \frac{1}{\epsilon^2 - 4\beta^2} = \int_0^1 \frac{dx}{\epsilon - 2\beta \cos \pi x} = \frac{1}{\sqrt{\epsilon^2 - 4\beta^2}}
\] (note, that the average \( \epsilon_b = 0 \) has been set up to 0) with the deterministic "Blue’s function"
\[
B^D = \sqrt{\frac{1}{\epsilon^2} + 4\beta^2}.
\] (4.43)

Evaluation of the deterministic \( G_{1N} \) element for this case leads, in the limit of \( (\epsilon_b - \epsilon)/2\beta \), to the usual McConnel result
\[
\lim_{N \to \infty} G_{1N} = 0.
\] (4.44)

Qualitative estimate of the transfer matrix for the “random plus deterministic” case follows now, according to the formula (3.31), determination of the inverse determinant for the full (diagonal random plus TBH deterministic) bridge Hamiltonian:
\[
G_{1N} = \left\{ \frac{(-1)^{N+1} \beta^{N-1}}{\det(H^D + H^R)} \right\}.
\] (4.45)
For \( \beta \) “large” \( \det \) is dominated by \( \beta \), giving \( \det = \beta^N \); for small \( \beta \) the determinant is dominated by the randomness of the diagonal elements in the bridge Hamiltonian. Thus naively, in the limiting case of “large” \( \beta \) (and for an infinite bridge) \( \beta \) in the numerator is expected to be
negligible compared to the \( \det \) leading to \( G_{1N} \) proportional to \( 1/\beta \). More careful analysis (see below) shows, that randomness always increases \( \gamma \), leading to the faster decay of the transfer matrix \( G_{1N} \) over the distance.

If randomness of \( \epsilon_b \) is chosen to be sampled with the semi-circle law,

\[
\varrho(\epsilon_b) = \frac{1}{2\pi\sigma^2}\sqrt{4\sigma^2 - \epsilon_b^2}
\]

(4.46)

which is equivalent to a random matrix model \([10,12,28]\) of the noisy contribution \( H^R \) to the bridge Hamiltonian, Green’s function associated with \( H^R \) takes the form (see eq. (4.37))

\[
G^R(\epsilon) = \frac{1}{\epsilon - \sigma^2 G^R(\epsilon)} = \frac{\epsilon \mp \sqrt{\epsilon^2 - 4\sigma^2}}{2\sigma^2}.
\]

(4.47)

The functional inverse of \( G^R \) is given by Blue’s function

\[
B^R(\epsilon) = \sigma^2 \epsilon + \frac{1}{\epsilon}
\]

(4.48)

and, after using the addition law \([1.41]\) leads to the following equation for the Green’s function of the system

\[
\sigma^4 G^4 - 2\epsilon^2 \sigma^2 G^3 + (\epsilon^2 - 4\beta^2) G^2 - 1 = 0.
\]

(4.49)

The end-points of the spectra may be calculated from the equation

\[
\frac{dG}{d\epsilon}|_{\epsilon=a} = \infty
\]

(4.50)

or, equivalently from the discriminant of the above equation. By introducing the rescaled variables

\[
\frac{\epsilon}{\beta} \rightarrow \epsilon, \quad \frac{\sigma}{\beta} \rightarrow \sigma, \quad \beta G \rightarrow G
\]

(4.51)

the discriminant (end-point condition) for the Pastur equation \((4.43)\) is

\[
4\epsilon^6 + (\sigma^4 - 48)\epsilon^4 + 16(12 - 5\sigma^2)\epsilon^2 - 16(4 + \sigma^4)^2 = 0.
\]

(4.52)

In the limit \( \sigma \rightarrow 0 \) that reduces to \((\epsilon^2 - 4)^3 = 0\), thus the support of the spectrum is one interval, with end-points \( \pm 2 \), while in the limit \( \sigma \rightarrow \infty \) \((\beta \rightarrow 0)\) one gets once again one interval with end-points \( \epsilon = \pm 2\sigma \). Generally, the discriminant equation has only one pair of real solution for any value of \( \sigma \).

The spectra for different values of \( \sigma \) is shown in Fig. 1. ‘Deterministic’ spectrum is divergent close to the end-points of the band. For an increasing value of the noise intensity \( \sigma \), the distribution \( \nu(\epsilon) \) flattens and, eventually changes from the bimodal function with two peaks located at the ends of the support to the unimodal distribution with a broad hump around the center of the support. The curvature around zero changes sign for a critical value of the noise intensity which can be found from \((4.49)\) analyzed around \( \epsilon = 0 \). With the scaling \((4.51)\) one gets then the critical value of \( \sigma_c \) in units of \( \beta \)

\[
\sigma_c = 12^{1/4} = 1.8612.
\]

(4.53)

\[
G_{1N}(\epsilon) = G^D_{1N}(\epsilon - \Sigma[G(\epsilon)])
\]

(4.54)

i.e., the same Pastur equation \((4.37)\) holds also for the non-diagonal elements of the total Green’s function. The general analysis of Eq. \((4.54)\) shows, that the solution \( \gamma = 0 \) can not be achieved any more for any combination of \( \epsilon_b \) and \( \beta \). However for “small” disorder the states with energies \((\epsilon_b - \epsilon)/2\beta \leq 1\) are stable with small decay coefficient (see Fig. 3). The most stable energies are sampled around \( \epsilon = 0 \) with decay coefficients

\[
\gamma = \log \left( \frac{1}{\sqrt{2}} \left( \sqrt{1+\sigma^4/2} - 1 \right) \right) \left( \sqrt{1+\sigma^4/2} + 1 \right)
\]

(4.55)

yielding \( \gamma = 0 \) only for vanishing randomness \((\sigma = 0)\).

In Fig. 3 one may note the cusp-like discontinuities around the end-points \( \epsilon_b \) of the spectrum. Their appearance may be understood analytically in the large \( \sigma \) limit, where by evaluating the resolvent \( G \) we neglect the deterministic part of the Hamiltonian. The resolvent then reads

\[
G^R(\epsilon) = \frac{\epsilon \pm \sqrt{\epsilon^2 - 4\sigma^2}}{2\sigma^2}
\]

(4.56)
with end-points $\epsilon_c = \pm 2\sigma$. Evaluating (4.54) and inserting it into (3.34) the expansion around the end-points $\epsilon_c$ for $\epsilon > \epsilon_c$ leads to

$$\gamma \approx \log \frac{\sqrt{\sigma^2 - 4}}{2} - \frac{\sqrt{\sigma}}{\sqrt{\sigma^2 - 4}}(\epsilon - \epsilon_c)^{1/2} + \ldots$$

(4.57)

showing the observed “cusp” around the end-point.

![Graph](image)

FIG. 2. Decay coefficient $\gamma$ as a function of energy for various intensities of the noise. $\beta$ has been set up to 1. The completely deterministic system ($\sigma = 0$) has $\gamma = 0$ for $|\epsilon| < 2$.

V. CONCLUSIONS

In this paper we have discussed briefly properties of a bridged electron transfer affected by site diagonal disorder in the bridge Hamiltonian. Instead of using the standard language of the Green’s function formalism, we have chosen to work with the functional inverse of the Green’s function (“Blue’s function”). The method stems from the powerful mathematical concept of free random variables [18,19] which has been shown to be an elegant tool in various applications of the random matrix theory [20–24,33].

Our model refers to the situation when the bridge is long enough to be considered infinite. Site diagonal disorder is assumed in the form of a random matrix model resulting in placing at each site of the bridging chain a random matrix with a semi-circular distribution of energies (Wegner model, [29]). That would correspond to a situation where the bridge energies are n-electron functions. Presence of noise extends and flattens the spectrum of the TBH Hamiltonian. For donor/acceptor energies sampled from the center of the TBH band, the noise increases the inverse localization length $\gamma$ and leads to a fast decay of the electronic coupling with the distance measured in bridge units. The kinetic rate becomes thus vastly reduced by the noise (note that our discussion relates only to the electronic part of the ET rate). The distribution of TBH energies has been shown to possess a noise-induced characteristics which depends on the value of the critical noise intensity $\sigma_c$. As expected [23,24,33], the diagonal disorder localizes the eigenfunctions of the TBH Hamiltonian resulting in the reduction of the electronic transfer matrix $T_{fi}$. Thus the diagonal noise reinforces the exponential decay of the effective coupling with increasing distance between the donor and acceptor.

The method of Blue’s function applied here is also suitable for nonhermitean ensembles of random matrices which are used in quantum theory of dissipation [14,22,33]. The paper discusses so far only the case of the hermitean ensemble. Extension of the formalism to models of dissipative transport will be presented elsewhere.

Acknowledgments

This project has been supported by the Deutsche Forschungsgemeinschaft, Bonn, the Funds der Chemischen Industrie, Frankfurt and by Hungarian grant FKFP126/97.
REFERENCES.

[1] T.J. Meyer and M.D. Newton, eds., Chem. Phys. (Special Issue), 176 (1993).
[2] A. Zee, Nucl. Phys. B474 (1996) 726.
[3] J. Ulstrup, Charge Transfer Processes in Condensed Media, (Springer Verlag, Berlin, 1979)
[4] R.A. Marcus and N. Sutin, Biochim. Biophys. Acta, 811 (1985) 265.
[5] S.S. Skourtis and J.N. Onuchic, Chem. Phys. Lett. 209 (1993) 171.
[6] H.M. McConnel, J.Chem.Phys. 35 (1961) 508.
[7] S. Larsson, J. Am. Chem. Soc. 103 (1981) 4034.
[8] J.W. Evenson and M. Karplus, J. Chem. Phys. 96 (1992) 5272.
[9] M. Kemp, A. Roiberg, V. Mujica, T. Wanta and M.A. Ratner, J. Phys. Chem. 100 (1996) 8349.
[10] M.L. Mehta, Random Matrices, (Academic Press, New York, 1991).
[11] M.C. Gutzwiller, Chaos in Classical and Quantum Mechanics, (Springer Verlag, Berlin, 1990).
[12] C.E. Porter, Statistical Theories of Spectra: Fluctuations, (Academic Press, New York, 1965).
[13] C. Mahaux and H.A. Weidenmüller, Shell Model Approach to Nuclear Reactions, (North Holland, Amsterdam, 1969).
[14] F. Haake, F. Izrailev, N. Lehmann, D. Saher and H.J. Sommers, Z. Phys. B88 (1992) 359.
[15] S. Iida, H.A. Weidenmüller and J.A. Zuk, Ann. Phys. 200 (1990) 219.
[16] A.D. Mirlin, A. Müller-Groeling and M.R. Zirnbauer, Ann. Phys. 236 (1994) 325.
[17] H.A. Weidenmüller and M.R. Zirnbauer, Nucl. Phys. B305 (1988) 339.
[18] D.V. Voiculescu, Invent. Math. 104 (1991) 201.
[19] R. Speicher, Math. Ann. 298 (1994) 611.
[20] E. Brézin and A. Zee, Phys. Rev. E49 (1994) 2588.
[21] R.A. Janik, M.A. Nowak, G. Papp, J. Wambach and I. Zahed, Phys. Rev. E55 (1997) 4100; R.A. Janik, M.A. Nowak, G. Papp and I. Zahed, Nucl. Phys. B501 (1997) 603.
[22] J. Feinberg and A. Zee Nonhermitean Random Matrix Models, e-print cond-mat/9703087
[23] E. Gudowska-Nowak, G. Papp and J.Brickmann, Chem. Phys. 220 (1997) 125.
[24] J.T. Chalker and Z. J. Wang, Phys. Rev. Lett. 79 (1997) 1797.
[25] C. Goldman, Phys. Rev. 43A (1991) 4500.
[26] E.P. Wigner and V. F. Weisskopf, Z. Phys. 63 (1930) 54.
[27] P.O. Löwdin, J. Math. Phys. 3 (1962) 969.
[28] J.M. Ziman, Models of disorder, Cambridge University Press, Cambridge, (1979).
[29] F. Wegner, Phys. Rev. B. 19 (1979) 783.
[30] F. Neu and R. Speicher, J. Stat. Phys. 80 (1995) 1279.
[31] R. Janik, M.A. Nowak, G. Papp and I. Zahed, Localization Transitions From Free Random Variables, e-print cond-mat/9705093.
[32] L.A. Pastur, Theor. Math. Phys. (USSR) 10 (1972) 67.
[33] N. Hatano and D.R. Nelson, Phys. Rev. Lett. 77 (1997) 570.
[34] J.B. Pendry, Adv. Phys. 43 (1993) 461.