

# Vibrational enhancement of the effective donor – acceptor Coupling

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The paper deals with a simple three sites model for charge transfer phenomena in an one-dimensional donor (D) – bridge (B) – acceptor (A) system coupled with vibrational dynamics of the B site. It is found that in a certain range of parameters the vibrational coupling leads to an enhancement of the effective donor – acceptor electronic coupling as a result of the formation of the polaron on the B site. This enhancement of the charge transfer efficiency is maximum at the resonance, where the effective energy of the fluctuating B site coincides with the donor (acceptor) energy.

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Molecular electronics is progressing so rapidly that it is now possible to do measurements and assembly at the level of individual or few molecules [1, 2]. Charge transport is known to occur in a wide range of linear chain molecules including the DNA double strand molecules. For DNA, it is believed that the charge transport phenomenon is involved in the protection of the DNA encoded information against the oxidative damage [3]. As the DNA molecule is essentially a dynamic structure on the time scale of charge transport, one expects that vibrational dynamics to play an important role for DNA electronics, and, in general, for any property of biological molecules because biological functions of life are associated with molecular motions but not to the static or dead structure (i.e., equilibrium positions of all atoms).

In this paper we are interested in an one-dimensional DNA wire or bridge (B) connecting a donor (D) and an acceptor (A) sites. Usually, the bridge consists of  $N$  sites with one state per site (see the abundant literature devoted to this issue in the Refs. [4–23]), and theoretical analysis of this problem requires to solve a system of  $N + 2$  non-linear coupled equations. Unfortunately, such a problem cannot be solved analytically for  $N \gg 1$ , and we have to recourse to numerical solution. However, many insights and essential features of the dynamics can already be gained and captured by studying a simple three sites: D–B–A. Generally speaking, the

interaction between the donor and acceptor involves all states of the bridging subsystem. This bridge mediated interaction can be characterized, under certain conditions, by a single energy dependent parameter – effective coupling – which plays the key role in the charge transfer. For small systems the phase coherence of charges is maintained over the entire system, and the quantum effects are crucial in determining the system properties. On the contrast, for the long  $N \gg 1$  bridges, fast relaxation processes result in a strong dephasing between charges in the system. Therefore, this leads to a rapid falloff of the off-diagonal elements of the density matrix such that the diagonal elements can be described by a set of kinetic equations [17, 24].

Our concern in this paper is to investigate a Hamiltonian model describing the D–A coupling under the presence of dynamic structural fluctuations. Such local fluctuations, including local vibrations, twist motions, radial deformations and hydrogen-bond stretching or opening, are known to strongly influence charge transfer in DNA molecules [25–30]. For simplicity, we consider a three sites D–B–A system where electronic degree of freedom is coupled to an effective local vibrational degree of freedom.

Let us assume that initially the charge is entirely localized on the donor site with energy  $\epsilon$ . Then owing to the non-zero overlapping integrals of the electronic wave functions between the two neighboring sites, the tunneling of the charge takes place from the donor to the acceptor site with the same energy. Denoting by  $\{|d\rangle, |b\rangle, |a\rangle\}$  the localized states on the donor, bridge and accep-

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tor, respectively, the Hamiltonian of the bridge - mediated charge transfer between the donor and acceptor acquires the form,

$$H = H_e + \frac{p^2}{2m} + \frac{m\omega^2 r^2}{2} + kr |b\rangle\langle b|, \quad (1)$$

in which the bare electronic part reads as,

$$H_e = \epsilon [|d\rangle\langle d| + |a\rangle\langle a|] + \epsilon_b |b\rangle\langle b| + v_{db} [|d\rangle\langle b| + |b\rangle\langle d|] + v_{ba} [|b\rangle\langle a| + |a\rangle\langle b|], \quad (2)$$

where  $\epsilon$  is the one-site energy of the donor and acceptor,  $\epsilon_b$  the one-site energy of the bridge,  $m$  ( $m \simeq 300$  amu) is the mass of the bridge base pair,  $r$  is its radial displacement in the localized vibrational mode with frequency  $\omega$ , the momentum  $p$  is conjugated to  $r$ , and  $k$  is the electron-localized vibration mode coupling constant. The localized bridge mode can be treated classically since the corresponding vibrational displacement amplitude is larger than zero point quantum fluctuations for characteristic DNA parameters [25–28] (see also the following).

The frequency of typical vibrations in DNA ranges  $\omega \simeq 10^{11} - 10^{12} \text{ s}^{-1}$ , and the scale of electronic overlap integrals between base pairs in DNA is  $v = \sqrt{2(v_{db}^2 + v_{ba}^2)} \simeq 0.2 \text{ eV}$  leading to an electronic characteristic frequency,  $v/\hbar \simeq 3 \cdot 10^{14} \text{ s}^{-1}$ . As a consequence of the small (adiabatic) parameter,  $v\omega/\hbar \ll 1$ , the slow vibrational and fast electronic motions can be decoupled. Therefore, to solve the problem of bridge-mediated charge transfer between the donor and the acceptor, we employ the adiabatic procedure to eliminate the slow vibrational motions and derive an effective Hamiltonian for fast electronic motions. To proceed, we take the wave function of the charge in the form,  $|\Psi(t)\rangle = c_d(t)|d\rangle + c_b(t)|b\rangle + c_a(t)|a\rangle$ , where  $c_n(t)$  are the time dependent amplitudes of the probability to have the charge at the  $n$ th site. From the Hamiltonian (1) we arrive at the following equations of motion for the quantum amplitude  $c_n(t)$ ,

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_d \\ c_b \\ c_a \end{pmatrix} = \begin{pmatrix} \epsilon & v_{db} & 0 \\ v_{db} & \epsilon_b + kr & v_{ba} \\ 0 & v_{ba} & \epsilon \end{pmatrix} \begin{pmatrix} c_d \\ c_b \\ c_a \end{pmatrix}, \quad (3)$$

and for the classical dynamic mode,

$$m \frac{d^2 r}{dt^2} = -m\omega^2 r - k |c_b|^2. \quad (4)$$

Next, we seek for stationary solutions of the form  $c_n(t) = c_n e^{-iEt/\hbar}$  oscillating with frequency  $E/\hbar$ . To work

with dimensionless quantities, we use from now the dimensionless variables  $u$ ,  $\sigma$  and  $\kappa$  defined in Table. Using  $c_n(t)$  in the equations of motions, we find that the stationary bridge displacement is  $r = -\kappa c_b^2$  and the stationary probability distribution is,

$$\begin{aligned} c_d^2 &= \eta^2 c_a^2, \\ c_b^2 &= 2u^2 / (1 + 2u^2), \\ c_a^2 &= 1 / [(1 + \eta^2)(1 + 2u^2)], \end{aligned} \quad (5)$$

where the root  $u$  satisfies the characteristic equation,

$$4u^4 + 4(\kappa^2 - \sigma)u^3 - 2\sigma u - 1 = 0. \quad (6)$$

Solutions of this equation provides the ground  $u_g$  plus one or three (depending upon values of  $\kappa$  and  $\sigma$ ) excited energies of the ‘‘polaron’’, i.e. the state created by the charge coupling with the DNA structural deformation. These stationary polaron solutions allows us to elimi-

**Definition of dimensionless variables**

definition	variable
energy scale	$v = \sqrt{2(v_{db}^2 + v_{ba}^2)}$
length scale	$\xi = \sqrt{v/m\omega^2}$
coupling asymmetry	$\eta = v_{db}/v_{ba}$
dimensionless polaron energy	$u = (E - \epsilon)/v$
dimensionless energy barrier	$\sigma = (\epsilon_b - \epsilon)/v$
reduced electron-vibration coupling	$\kappa = k\xi/v$

nate from (1) the structural deformation  $r$  and to obtain the effective Hamiltonian for the charge transfer as,

$$\begin{aligned} H_{\text{eff}} &= \frac{1}{v} (H_e - \epsilon \hat{1}) = \Delta(u) |b\rangle\langle b| + \\ &+ \frac{\eta}{\sqrt{2(1 + \eta^2)}} [|d\rangle\langle b| + |b\rangle\langle d|] + \\ &+ \frac{1}{\sqrt{2(1 + \eta^2)}} [|b\rangle\langle a| + |a\rangle\langle b|], \end{aligned} \quad (7)$$

where,  $\Delta(u) = \sigma - \kappa^2 c_b^2(u)$ , is the renormalized effective energy of the bridge due to electron - vibration coupling, and  $\hat{1}$  is the unit matrix. To calculate the effective charge coupling between the donor and the acceptor, we have to solve first the time dependent problem to determine the probability of charge transfer defined as,  $P_{d \rightarrow a}(t) = |\langle a|\Psi(t)\rangle|^2$ , where  $|\Psi(t)\rangle$  is the solution of the Schrödinger equation,

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = H_{\text{eff}} |\Psi(t)\rangle,$$

with the initial condition,  $|\Psi(0)\rangle = |d\rangle$ . It is easy to show that, when  $t \rightarrow \infty$  we have  $P_{d \rightarrow a}(t) \simeq k_{da} t$ , where

the charge transfer rate  $k_{da}$  is given by the Fermi Golden rule,

$$k_{da} = \frac{2\pi}{\hbar} |H_{da}|^2 \times \begin{cases} \delta(E_2(u) - E_1(u)); & \sigma \geq \kappa^2 c_b^2 \\ \delta(E_3(u) - E_1(u)); & \sigma \leq \kappa^2 c_b^2 \end{cases}, \quad (8)$$

with the (dimensionless) effective donor – acceptor coupling [18],

$$|H_{da}|^2 = \frac{\eta^2}{4(1 + \eta^2)^2} \times \begin{cases} 1/[(E_3(u) - E_1(u))(E_3(u) - E_2(u))]; & \sigma \geq \kappa^2 c_b^2 \\ 1/[(E_1(u) - E_2(u))(E_3(u) - E_2(u))]; & \sigma \leq \kappa^2 c_b^2 \end{cases}, \quad (9)$$

where  $E_i(u)$  are the eigen-energies of  $H_{\text{eff}}$  given by  $E_1(u) = 0$  and  $2E_{2,3}(u) = \Delta \mp \sqrt{\Delta^2 + 2}$ . Finally, we end up with the effective D-A coupling given by,

$$|H_{da}(u, \eta, \sigma, \kappa)|^2 = \frac{\eta^2}{2(1 + \eta^2)^2 \sqrt{\Delta^2 + 2}} \times \frac{1}{[|\Delta| + \sqrt{\Delta^2 + 2}]}, \quad (10)$$

and the ratio  $\rho$ , allowing to measure the effect of vibrations on the D-A coupling, reads:

$$\rho(u, \sigma, \kappa) = \frac{|H_{da}(u, \eta, \sigma, \kappa)|^2}{|H_{da}(u, \eta, \sigma, 0)|^2} = \left[ \frac{|\sigma| + \sqrt{\sigma^2 + 2}}{|\Delta| + \sqrt{\Delta^2 + 2}} \right] \times \left[ \frac{\sigma^2 + 2}{\Delta^2 + 2} \right]^{1/2}. \quad (11)$$

The expressions (10) and (11) are the main results of this paper. They provide close formulas for evaluating how the dynamical disorder affects the effective donor-acceptor coupling in various situations. As a direct applications of our main findings, we consider the following illustrative examples.

**Charge density versus polaron energy.** It results from Eq.(5) that the charge densities on the donor, bridge and acceptor are even functions of the polaron energy  $u$ . For all  $u$ , the ratio of the density of the donor to that of the acceptor is equal the square of the asymmetry energy  $\eta$  (see the Table). For  $u = 0$ , there is no charge on the bridge site, and the charge density is distributed between the donor and acceptor sites in proportion of  $\eta$ . In contrast, for the limits of very high (or low) polaron energy when  $|u|$  gets larger, the charge density decreases considerably on the donor and acceptor sites while it gets higher on the bridge site leading hence to small charge transfer efficiency. These features are illustrated in Fig.1 for the energy asymmetry parameter

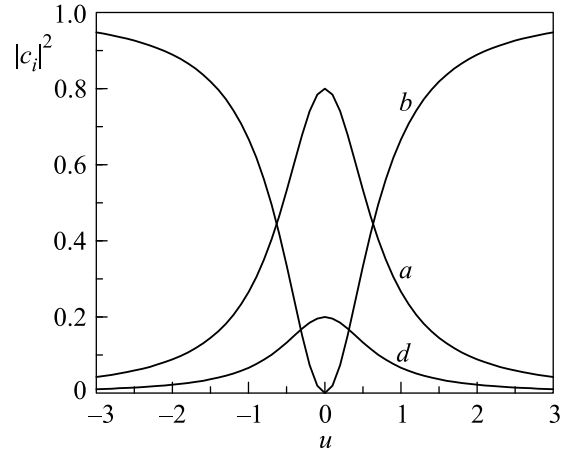


Fig.1. Stationary charge density in Eq.(5) versus energy for the coupling asymmetry  $\eta = 0.5$ . The quoted letters  $d$ ,  $b$ , and  $a$  stand for the donor, bridge and acceptor, respectively

$\eta = 0.5$ . Likewise, at the resonance  $u_m$  where the renormalized effective energy of the bridge is equal to zero (the donor/acceptor energy),

$$\Delta(u_m) = 0 \implies u_m = \pm \frac{\sqrt{\sigma}}{\sqrt{2(\kappa^2 - \sigma)}}, \quad (12)$$

the distribution of charge density reduces to,

$$\begin{aligned} c_d^2(u_m) &= \eta^2 c_a^2(u_m), \\ c_b^2(u_m) &= \sigma / \kappa^2, \\ c_a^2(u_m) &= [1 - c_b^2(u_m)] / (1 + \eta^2). \end{aligned} \quad (13)$$

At this resonance point, the charge density on the bridge site decreases either upon approaching to the bare resonance for  $\sigma \rightarrow 0$  or by increasing the electron-vibration coupling parameter  $\kappa$  above  $\sqrt{\sigma}$ .

**Effective D-A coupling versus  $u$ .** The effective D-A coupling scales as,  $|H_{da}| \sim 1/\Delta$  for  $\Delta \gg 1$ . However, at the resonance  $\Delta = 0$  defined in Eq.(12), the  $|H_{da}(u, \eta, \sigma, \kappa)|^2$ , and thus the ratio  $\rho(u, \sigma, \kappa)$ , attain their maxima given by,

$$|H_{da}(u_m, \sigma, \kappa)|^2 = \frac{\eta^2}{4(1 + \eta^2)^2}, \quad (14)$$

and

$$\rho(u_m, \sigma, \kappa) = \frac{(\sigma + \sqrt{\sigma^2 + 2}) \sqrt{\sigma^2 + 2}}{2}. \quad (15)$$

Simple inspection of this equation shows two characteristic features. First, at the resonance the effective D-A coupling is enhanced by the coupling to structural dynamics, and second, as it is illustrated in the Fig.2, the

enhancement factor  $\rho$  of the effective D-A coupling due to electron-vibration interactions increases with energy barrier  $\sigma$ . To rationalize these observations in terms of the polaron energy and electron-vibration coupling, we have depicted in Fig.2 the ratio  $\rho(u, \sigma, \kappa)$  as a function of  $u$  for increasing values of  $\sigma$  and  $\kappa$ . Two different regimes can be distinguished:

- $\kappa < \sqrt{\sigma}$ : below the resonance value, the effective D-A coupling is a monotonic increasing function of the polaron energy  $|u|$ ;
- $\kappa \geq \sqrt{\sigma}$ : the effective D-A coupling increases for  $|u| < |u_m|$ , attains its maximum at the resonance  $|u| = |u_m|$ , and decreases for  $|u| > |u_m|$ . As a consequence of  $|H_{da}(u, \sigma, 0)| \sim 1/\sigma$ , both the maximum of  $\rho$  at the resonance and its limit at high  $|u|$  increase with  $\sigma$ .

**Effective D-A coupling versus  $\kappa$ .** As we have discussed above and illustrated in Fig.2, the electron-vibration may lead to an increase or decrease of the effective D-A coupling depending on the value of  $|u|$  and the regime of  $\sigma$ . Similarly, Fig.3 displays the enhancement factor  $\rho$  at the polaron ground state as a function of the electron-vibration coupling  $\kappa$ . It is clear that there is a certain threshold value  $\kappa_c(u_g)$  below which the electron-vibration coupling leads to enhancement of the effective D-A coupling, and above which the effective D-A coupling is drastically reduced affecting hence the charge transfer efficiency.

As above, two different regimes can be distinguished:

- $\sigma \leq 1$ : equation (6) has two distinct roots corresponding to the ground and excited states, respectively. The maximum enhancement,  $\rho(u_m, \sigma, \kappa_c)$  given by Eq.(15), is attained at the resonance  $\Delta = 0$ , where  $u_g = -\sqrt{2}/2$  (and the excited state,  $-u_g$ ) and  $\kappa_c(u_g) = \sqrt{2}\sigma$ , obtained from the combination of Eqs.(6) and (12). In this regime, the ground state coincide with the resonant energy,  $u_g = u_m$ ;
- $\sigma > 1$ : there is an interval,  $\kappa_c(u_g) \leq \kappa \leq \kappa_{\max}$ , within which Eq.(6) admits four distinct roots (the lowest one corresponding to the ground state) and out of which it has two distinct roots. In this case, the ground state is no longer resonant,  $u_g \neq u_m$ , but two excited states coincide with the resonant energies given by  $u_m = \pm\sqrt{2}/2$ . As a result, the maximum enhancement  $\rho(u_g, \sigma, \kappa) < \rho(u_m, \sigma, \kappa_c)$  as  $\Delta(u_g) \neq 0$ . For instance, for  $\sigma = 2$ , the four distinct roots interval is  $1.9336 \leq \kappa \leq 2.175$  with  $\kappa_c = 1.9336$  and the maximum enhancement

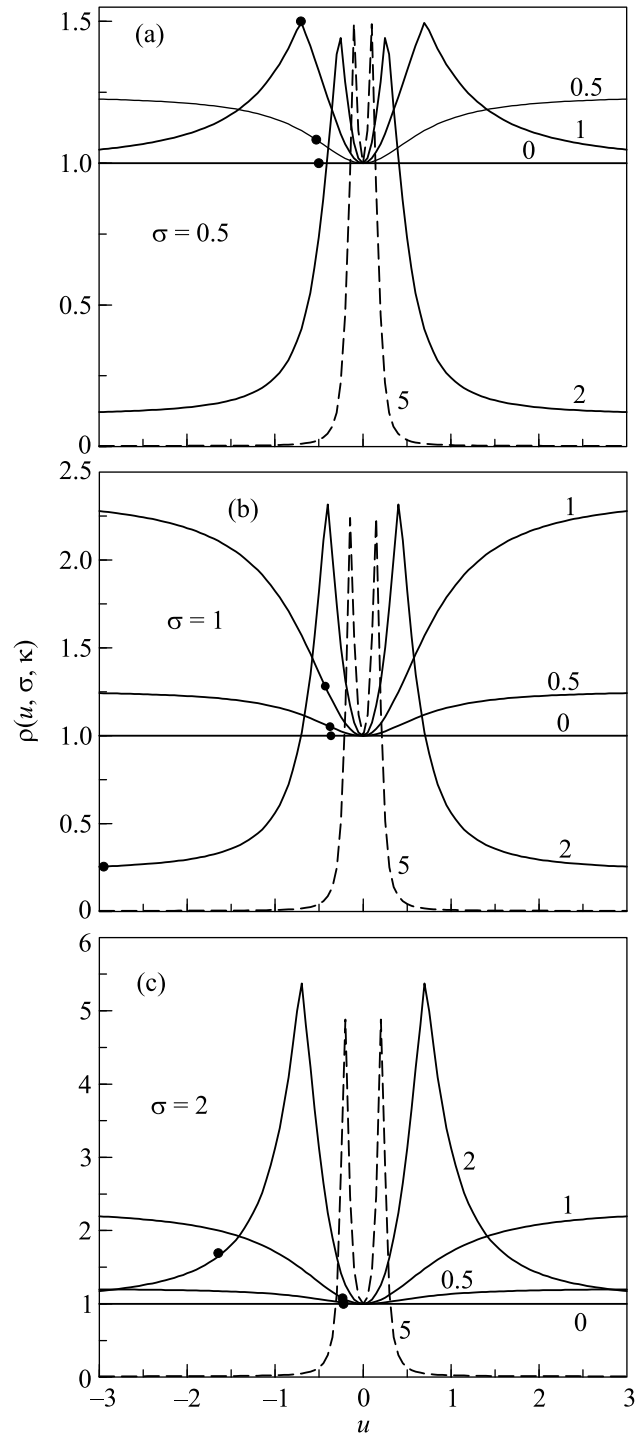


Fig.2. Effective coupling ratio in Eq.(11) as a function of the energy. Filled circles correspond to  $\rho(u_g, \sigma, \kappa)$  at the ground state energy  $u_g$ . The quoted numbers correspond to the electron-vibration coupling values, i.e.,  $\kappa = 0, 0.5, 1, 2, 5$

$\rho(u_g, \sigma, \kappa_c) = 3.198$  is obtained for  $u_g = -1.097$ . At the resonance  $\Delta = 0$  for  $\sigma = 2$ , we have  $\kappa = 2$ ,  $u_g = -1.707$ ,  $\Delta(u_g) = -\sqrt{2}$  and  $\rho(u_g, \sigma, \kappa) = 1.596$ .

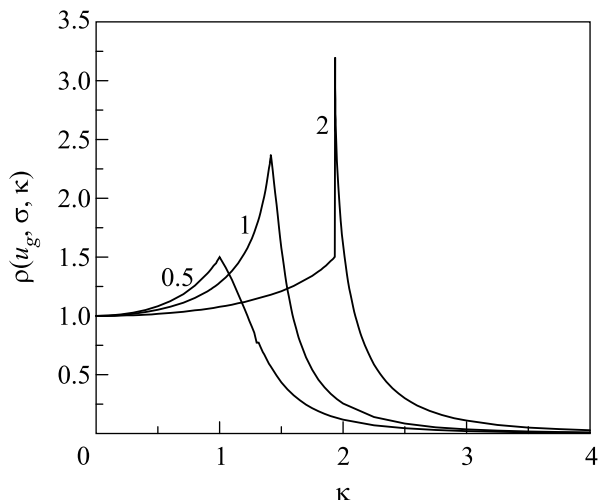


Fig.3. Effective coupling ratio in Eq.(11) at the ground state energy  $u_g$  as a function of the electron-vibration coupling. The quoted numbers correspond to the energy barrier values, i.e.,  $\sigma = 0.5, 1, 2$

In summary, we have shown that the electronic coupling with the vibration dynamics of the bridge results in a formation of a polaron that may, under certain conditions, leads to an enhancement of the charge transfer efficiency. Figures 2 and 3 show that the enhancement factor  $\rho$  is greater than one for a wide range of the energy barrier  $\sigma$  and the electron-vibration coupling  $\kappa$ . These findings are very suggestive for the issue of charge transport assisted by structural dynamical along the DNA chain. To study the basic mechanism of vibration enhancement of charge transport we have focused in this work on the simple three sites model with a single harmonic structural dynamic mode (reaction coordinate). Meanwhile, the method employed in this work is not limited to this model and the extension of the theory to several sites and anharmonic reaction coordinates (see e.g., Refs.[27, 28]), and several resonance states can be handled within the framework developed in Ref. [18]. Nevertheless, further theoretical studies need to be conducted along the ideas outlined above in order to gain a better understanding of charge transport properties in biological systems and technological applications of significant importance.

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