Bridge-mediated Donor-Acceptor Effective Coupling: Exact theoretical description.

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An exact expression of the bridge-mediated donor-acceptor effective coupling, \( H_{da} \), is derived. For systems represented by a tight-binding Hamiltonian with nearest-neighbor interactions, we show that \( |H_{da}|^2 \) is equal to the product over all square of nearest-neighbor couplings divided by an appropriate product of level spacing of eigen energies of the Hamiltonian. Results of this calculation are compared to those obtained by perturbative approaches and some drawbacks of the latter are pointed out.

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There are many physical, chemical and biological processes involving transfers of excitations between electrodes or from a donor (D) to an acceptor (A), through a mediated (environmental) composite bridge (B), that can be described formally by the reaction scheme, \( D^* - B - A \rightarrow D - B - A^* \). Such processes include, for instance, charge transfer, where charge are transferred from the donor to the acceptor through intermediate states connected them, or in energy transfer [1, 2]. The quantity of interest for such donor-bridge-acceptor systems is the effective coupling \( H_{da} \) between the donor and the acceptor which carries the dominant distance dependence of charge transfer efficiency, and that enters the transfer rate constant as a principal factor among others. Although the problem of computing the effective coupling is general to many processes, to be specific we will present our calculations within the framework of charge transfer. Recently, a number of experimental groups have reported measurements of the DNA charge transfer, and besides several theoretical models have been developed (see e.g., [3, 4], more recent review papers [5, 6], and references herein). It is however disappointing that the results obtained so far using different approaches are not the same and even irreconcilable. It would therefore seem appropriate at this time to put the theoretical treatment on a firm footing to analyze more accurately all essential ingredients of the charge transfer phenomena, and among those the principal one - the effective \( D - A \) coupling \( H_{da} \) is our concern in this paper. In what follows we derive an exact close analytical expression for \( H_{da} \). It is not only of intellectual interest but also of relevance to gain further insight into the nature of DNA charge transfer, since comparing our exact expression and known in the literature results, one can estimate the accuracy and reliability of various theoretical approximations.

For a two-state system where the system is initially prepared in the donor state, the probability of finding the system in the acceptor state is given by,

\[
P_{d\rightarrow a}(t) = \sin^2 \left( \frac{(E_+ - E_-)t}{2\hbar} \right), \tag{1}
\]

where \( E_\pm \) (with \( E_+ > E_- \)) are the splitting eigenenergies of the Hamiltonian describing the system. Using the relation, \( \lim_{t\to\infty} \sin^2(\pi x/t) = \pi t \delta(x) \), yields,

\[
\lim_{t\to\infty} P_{d\rightarrow a}(t) \approx k_{da}t \text{ where } k_{da} \text{ is the rate constant given by the Golden rule, } k_{da} = \frac{\pi}{\hbar} |H_{da}|^2 \delta(E_+ - E_-), \text{ where } H_{da} = (E_+ - E_-)/2 \text{ is the effective donor-acceptor coupling of the problem. For multi-state systems, several authors } [2, 9, 10, 11, 12, 13, 14, 15] \text{ have used various approaches (perturbation theory, Löwdin’s matrix partitioning technique, Green’s function method) to derive an expression for the effective coupling. These approaches consist of mapping the multi-state eigenvalue problem onto the eigenvalue problem for the two-state system in order to determine the approximate splitting energies } E_\pm \text{ and } H_{da} \text{ as above. Accordingly, it is well established that the effective coupling between the donor and the acceptor can be expressed in terms of the Green’s function of the bridge evaluated for the donor/acceptor energy } [12, 13].

To move further on smoothly and without loss of generality, we consider a \( N + 2 \) system, \( \{|n\} \) denoting the localized states on the the donor (\( n = 0 \)), bridge (\( N \) sites with one state per site, denoted \( n = 1, 2, \ldots, N \)) and acceptor (\( n = N + 1 \)). As pioneered by McConnell [2], we deal with the tight-binding (Hückel) Hamiltonian describing the charge transfer from a donor to an acceptor through the bridge with site energies \( \varepsilon_n \) and nearest-neighbor interactions \( v_n \) between sites,

\[
H = \begin{pmatrix}
\varepsilon_0 & v_1 & 0 & 0 & \cdots \\
v_1 & \varepsilon_1 & v_2 & 0 & \cdots \\
0 & \ddots & \ddots & \ddots & 0 \\
\vdots & 0 & \varepsilon_N & v_{N+1} \\
0 & \cdots & 0 & \varepsilon_{N+1}
\end{pmatrix} . \tag{2}
\]

For this Hamiltonian (in which \( \varepsilon_0 = \varepsilon_{N+1} = \varepsilon \)), the splitting energies \( E_\pm \) can be obtained as roots of the equations [11],

\[
E_\pm - \varepsilon = -a(E_\pm) \pm \sqrt{b(E_\pm)^2 + 4c(E_\pm)} \tag{3}
\]

where, \( a(E) = v_1^2 G_{11}(E) + v_{N+1}^2 G_{NN}(E) \), \( b(E) = v_1^2 G_{11}(E) - v_{N+1}^2 G_{NN}(E) \), \( c(E) = v_1^2 G_{11}(E) + \)
with the initial condition, $|\Psi(t)\rangle >$ is the solution of the Schrödinger equation along with the Golden rule. To proceed, we solve the time dependent problem to determine the probability of charge transfer defined as, $P_d \rightarrow a(t) = |< 0 |\Psi(t)\rangle |^2$, where $|\Psi(t)\rangle >$ is the solution of the Schrödinger equation,
\[
\frac{i\hbar}{\Delta}\frac{d}{dt}|\Psi(t)\rangle > = H|\Psi(t)\rangle >
\]
with the initial condition, $|\Psi(0)\rangle > = |0\rangle >$. If we denote by $|\phi_n\rangle >$ and $E_n$ (with, $n = 0, 1, \cdots, N + 1$) the eigenstates and associated eigen energies of a given $(N + 2) \times (N + 2)$ Hamiltonian, one can show that the transition probability reads as,
\[
P_d \rightarrow a(t) = -\sum_{n=0}^{N} \sum_{m=n+1}^{N+1} 4 < N + 1 |\Pi_n| 0 > \times < N + 1 |\Pi_m| 0 > \sin^2\left(\frac{(\Delta E_{n,m}) t}{2\hbar}\right),
\]
where, $\Delta E_{n,m} = E_n - E_m$, is the eigen energy spacing and, $\Pi_n = |\phi_n\rangle > \langle \phi_n|$, is the projection operator on the eigenstate $|\phi_n\rangle >$. Equation (5) is a generalization of Eq. (1) to many state systems. As $t \rightarrow \infty$, the leading term in $P_d \rightarrow a(t)$ will be associated to the smallest energy spacing, $|\Delta E_{l+1,l}|$, and defining hence the index $l$. Likewise, proceeding as done below Eq. (1), we find for Eq. (5) that, $\lim_{t \rightarrow \infty} P_d \rightarrow a(t) \approx k_{da}$, with the rate constant, $k_{da} = \frac{2\pi}{\hbar} |H_{da}|^2 \delta(E_{l+1} - E_l)$, where the effective donor-acceptor coupling is given by,
\[
|H_{da}|^2 = -< N + 1 |\Pi_l| 0 > \times < N + 1 |\Pi_{l+1}| 0 > |\Delta E_{l,l+1}|^2.
\]
This expression provides a quite general and close formula for computing the effective coupling in various contexts.

Our main result can be formulated as follows. For a given Hamiltonian, compute the eigen energy spectrum $E_n$, sort the $E_n$ in ascending (or descending) order, and identify the index $i^n$ defined such that $|\Delta E_{l+1,l}| = \min |\Delta E_{n,m}| : n, m \in \text{spectrum}$. Next, determine the associated eigenstates $|\phi_n\rangle >$ and $|\phi_{l+1}\rangle >$, and finally compute the effective coupling according to Eq. (6). In addition, an approximate expression of Eq. (6) can also be derived by using the perturbation theory or Green’s function technique for the projection operators $\Pi_l$ and eigen energies $E_l$. We expect that the $|H_{da}|$ derived this way to better approximation because of the smallest eigen energy spacing $\Delta E_{l,l+1}$.

Now, to illustrate the results in Eqs. (5) and (6), we derive explicitly the above expression for a tight-binding Hamiltonian as given in Eq. (4). To this end, we consider the wave function of the form, $|\Psi(t)\rangle > = \sum_{n=0}^{N+1} c_n(t)|n\rangle >$, where $c_n(t)$ are the time dependent amplitude of the probability of charge at the $n$th site. This yields the following system of equations,
\[
\begin{align*}
\frac{i\hbar}{\Delta} \frac{d c_0}{dt} &= \varepsilon_0 c_0 + v_1 c_1 \\
\frac{i\hbar}{\Delta} \frac{d c_n}{dt} &= v_n c_{n-1} + \varepsilon_n c_n + v_{n+1} c_{n+1}; \quad 1 \leq n \leq N \\
\frac{i\hbar}{\Delta} \frac{d c_{N+1}}{dt} &= v_{N+1} c_N + \varepsilon_{N+1} c_{N+1}
\end{align*}
\]
with the initial condition, $c_n(0) = \delta_{n0}$. We define the Laplace transform $\tilde{f}(s) = \int_0^\infty f(t) e^{-sf} dt$ of any function $f(t)$. Laplace transforming Eq. (7) and solving the resulting equation, we obtain the recurrence formula,
\[
\frac{i\varepsilon c_{n+1}}{\Delta} \Delta_{n-1} \tilde{c}_{n+1}(s) + \Delta_n \tilde{c}_n(s) = \prod_{m=1}^{n} \left( -\frac{i\varepsilon_m}{\hbar} \right) \Delta_{n+1}
\]
where $\Delta_n = (s + i\varepsilon_n/\hbar)\Delta_{n-1} - (i\varepsilon_n/\hbar)^2 \Delta_{n-2}$ with $\Delta_{-1} = 1$ and $\Delta_0 = (s + i\varepsilon_0/\hbar)$. If $E_n (n = 0, 1, \cdots, N+1)$ denotes the eigen energies of $H$, we have: $\Delta_{N+1} =$
the amplitude, it follows that the smallest energy spacing is given by,
\[ \Delta E_{1,0} = \frac{1}{\Delta N+1} \prod_{m=1}^{N+1} \left( -\frac{i v_m}{\hbar} \right) \prod_{n=0}^{N+1} (s + i E_n/\hbar). \]
After inverse Laplace transforming this expression we find that the probability \( P_{d \to n}(t) \) is given by Eq. (5) with the amplitude,
\[ <N + 1|\Pi_n|0> = \prod_{i=1}^{N+1} \frac{v_i}{(E_i - E_j) \prod_{j=0, j\neq n}^{N+1} (E_i - E_j)}. \]
Now, using the formula in Eq. (5) leads to the following expression for the effective coupling,
\[ |H_{da}|^2 = \prod_{i=1}^{N+1} v_i^2 \prod_{j=0}^{N+1} (E_i - E_j) \prod_{j\neq i}^{N+1} (E_i - E_j), \]
where the index “\( l \)” is defined such that \( |\Delta E_{l+1,t}| \) is the smallest energy spacing of the eigen energy spectrum of the entire Hamiltonian. For this kind of Hamiltonian, the computation of the effective coupling is reduced to the determination of eigen energies of the system Hamiltonian.

As a direct application of the formula in Eq. (11), we consider the following illustrative examples in which the energies of the donor and acceptor are both equal, \( \varepsilon_0 = \varepsilon_{N+1} = \varepsilon \).

### System with 2 + 2 Levels:

The simplest example which can worked out analytically is the one where the bridge is reduced to a single site (i.e., \( N = 1 \)). In this case, the Hamiltonian in Eq. (4) reduces to a \( 3 \times 3 \) matrix whose eigen energies are given by,
\[ \begin{align*}
E_0 &= \frac{\sqrt{(\varepsilon - \varepsilon_1)^2 + 4(v_1^2 + v_2^2)}}{2} \\
E_1 &= \varepsilon \\
E_2 &= \frac{\sqrt{(\varepsilon + \varepsilon_1)^2 + 4(v_1^2 + v_2^2)}}{2}
\end{align*} \]
It follows from this that the smallest energy spacing is \( \Delta E_{1,0} \) with \( l = 0 \) for \( \varepsilon_1 > \varepsilon \) and \( \Delta E_{2,1} \) with \( l = 1 \) for \( \varepsilon_1 < \varepsilon \). Applying the formula in Eq. (11), we get:
\[ |H_{da}|^2 = \frac{v_1^2 v_2^2}{4[(v_1 + v_2)^2 + v_2^2]}. \]

This is to compare with \( |H_{da}^{(1)}| = v_1 v_2 /|\varepsilon_1 - \varepsilon| \), obtained from using the approximate formula in Eq. (11).

### Degenerate System with 2 + 2 Levels:

An other interesting example where the formula in Eq. (11) fails to provide a finite value is, for instance, a bridge of size \( N = 2 \) with sites energies equal to the donor/acceptor energy, \( \varepsilon_1 = \varepsilon_2 = \varepsilon \). In this case, the eigen energies of the \( 4 \times 4 \) Hamiltonian matrix are given by,
\[ \begin{align*}
E_0 &= \varepsilon - \lambda_+/2 \\
E_1 &= \varepsilon - \lambda_-/2 \\
E_2 &= \varepsilon + \lambda_-/2 \\
E_3 &= \varepsilon + \lambda_+/2
\end{align*} \]
where \( \lambda_+ = \sqrt{2(v_1^2 + v_2^2 + v_3^2)} \pm 2 \sqrt{(v_1^2 + v_2^2 + v_3^2)^2 - 4v_1^2v_3^2} \), with \( \lambda_+ > \lambda_- \). Here, \( l = 0 \) (or \( l = 2 \)) corresponding to the smallest energy spacing \( \Delta E_{1,0} \) (or \( \Delta E_{3,2} \)). As a result, we find:
\[ |H_{da}|^2 = \frac{v_1^2 v_2^2 v_3^2}{\Delta E_{0,2} \Delta E_{1,2} \Delta E_{0,3} \Delta E_{1,3}} = \frac{v_1^2 v_2^2 v_3}{4[(v_1 + v_2)^2 + v_2^2]}. \]

### System with 2 + 2 Levels:

As a last example, we consider the situation where the bridge of size \( N \) is composed of sites with energies, \( \varepsilon_n = \varepsilon_b \) and coupling, \( v_n = v \). In this case, the determinant \( \Delta_n \) for the given energies satisfies the recurrence relation,
\[ \begin{align*}
\Delta_n &= (\varepsilon_b - E)\Delta_{n-1} + v^2\Delta_{n-2} = 0 ; n \leq N \\
\Delta_{N+1} &= (\varepsilon - E)\Delta_N + v^2\Delta_{N-1} = 0
\end{align*} \]
with \( \Delta_1 = 1 \) and \( \Delta_0 = \varepsilon - E \). Introducing the variables, \( \varepsilon_b - E = 2v x \) and \( \sigma = (\varepsilon_b - \varepsilon)/v \), one can show that,
\[ \begin{align*}
\Delta_n &= v^{n+1} [U_{n+1}(x) - 2\sigma U_n(x)] ; n \leq N \\
\Delta_{N+1} &= 2v(x - \sigma)\Delta_N - v^2\Delta_{N-1} = 0
\end{align*} \]
where \( U_n(\cos \theta) = \sin [(n+1)\theta]/\sin \theta \) is the trigonometrical representation for the Chebyshev polynomials of the second kind that satisfy the recurrence relation, \( U_{n+1}(x) = 2xU_n(x) + U_{n-1}(x) = 0 \) [13]. The characteristic equation for the eigen energies reads, \( \Delta_{N+1} = 0 \), i.e.,
\[ U_{N+2}(x) - 2\sigma U_{N+1}(x) + \sigma^2 U_N(x) = 0. \]

As a polynomial of degree \( N + 2 \) in \( x \), this equation has \( N + 2 \) roots \( x_k^{(N)}(\sigma) \), \( k = 1, 2, \cdots, N + 2 \), which could be found numerically. To each root corresponds an eigen energy, \( E_{k-1}(\sigma) = \varepsilon_b - 2v x_k^{(N)}(\sigma) \). One can convince ourselves when the eigen energies are arranged in ascending order (i.e., \( E_0 < E_1 < \cdots < E_{N+1} \), a choice for the smallest energy spacing is \( E_1 - E_0 \) (i.e., \( x_1^{(N)} - x_2^{(N)} \)) so that \( l = 0 \). In this case, the effective coupling is given
As a check, Eq. (18) reduces for \( N = 1 \) to, 8\( x^3 - 8\sigma x^2 + 2(\sigma^2 - 2)x + 2\sigma = 0 \), whose solutions are: 
\[ x_1^{(1)} = \left[ |\sigma| + \sqrt{\sigma^2 + 8} \right] / 4, \quad x_2^{(1)} = |\sigma|/2 \quad \text{and} \quad x_3^{(1)} = \left[ |\sigma| - \sqrt{\sigma^2 + 8} \right] / 4. \]

Using these roots in Eq. (16) leads to Eq. (18).

The evaluation of \( x_k^{(N)}(\sigma) \) in explicit terms does not seem to be feasible. However, for \( \sigma = 0 \) or \( \sigma = \pm 1 \), Eq. (18) has the exact solutions (for \( k = 1, 2, \cdots, N + 2 \)),

\[ x_k^{(N)}(0) = \cos \left( \frac{k\pi}{N+3} \right), \quad (20) \]

\[ x_k^{(N)}(\pm 1) = \cos \left( \frac{(k-1)\pi}{N+2} \right). \quad (21) \]

For comparison, the effective coupling obtained by using the approximate formula in Eq. (14) is [12, 13],

\[ |H_{da}^{(1)}| = \frac{2^{N+1} \sqrt{\sigma^2 - 4}}{(\sigma + \sqrt{\sigma^2 - 4})^{N+1} - (\sigma - \sqrt{\sigma^2 - 4})^{N+1}} \quad (22) \]

In contrast to Eq. (19), this function diverges for \( \sigma = 0 \) and values \( \sigma_k^{(N)} = 2 \cos \left[ k\pi/(N+1) \right] \), \( k = 1, 2, \cdots, N \), corresponding to the donor/acceptor energy equal to eigen energies of the isolated bridge, \( E_{k-1}^{\text{bridge}} = \varepsilon_b - 2 \cos \left[ k\pi/(N+1) \right] \). Numerical comparison of Eq. (22) with the exact expression in Eq. (19) shows that Eq. (22) overestimates the value of the effective coupling.

To sum up, we have derived a quite general and close formula in Eq. (9) for computing the effective donor-acceptor coupling for a given Hamiltonian. For a tight-binding Hamiltonian with nearest-neighbor interactions, Eq. (14) reduces to Eq. (11), and the computation of the effective coupling is reduced to the determination of eigen energies of the system Hamiltonian. The presented results can be extended in several directions to the more general processes of electron transfer between two reservoirs of states, exemplified by the molecular vibrational levels associated with the donor and acceptor sites connected by a molecular wire. It requires a set of different methods with specific approximations on certain scales of length and time but the coupling \( H_{da} \) calculated in this paper is the indispensable entry point into such more realistic study.

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