Tight-binding study of interaction time in molecular switches

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A characteristic switching time, associated with an impurity embedded in a tight-binding polyene chain, is developed. The modulated-energy traversal time, derived for potential models, is modified to the tight-binding situation. Since the traversal time takes into account the physical distance propagated, which is a meaningless concept in the context of the tight-binding model, we obtain an interaction time that measures the delay in tunnelling through the impurity site. The switching time is discussed in terms of the impurity-parameter space. [S0163-1829(96)02625-2]

I. INTRODUCTION

Since an electron in a quantal system is described by a delocalized wave function, and is subject to the limitations imposed by the uncertainty principle, it is difficult to associate a characteristic time over which the electron can be said to be located within a particular region. Various attempts have been made to associate a characteristic time to the system of an electron tunneling through a potential barrier.[1–6] Part of the difficulty is that the characteristic times derived describe different aspects of different physical situations, which complicates comparison among theoretical derivations and with experimental results.

We do not intend to investigate the appropriateness of these derivations, or their interpretations, but rather use the applicability to the system in question as the criterion for selecting the *traversal time*[7,8] to characterize our switch, which we describe as an impurity embedded in a polyene chain. We use a simple metal-like model[9] of the system to illustrate the method for extracting the switching time. Applications to more realistic models will be the basis of future work.

Previous analysis of this system,[9,10] via the tight-binding approximation (TBA), provides ready access to the *propagation matrix* **P**, the *transfer matrix* **T**(E), and the *transmission coefficient* $t(E)$, through the impurity. This information allows one to calculate either the time delay[11,12] based on collision theory, or the traversal time[3,7,13] appropriate to tunnelling situations. Since the relevant time through a switching mechanism is when it is on, it is the latter situation which is appropriate, and so a characteristic time for the switch based on the Martin-Landauer (ML) derivation.[7] Since the definition of the transmission coefficient in the TBA does not contain the phase change, exp(ikL), across the region, the ML formula[7] does not produce a traversal time, nor will the TBA calculation reduce to the transit time under WKB conditions.

Thus, it is this phase change that allows us to convert the *complex transmission coefficient* from the potential model to the tight-binding one, viz.,

$$\mathbf{t}(E) = \mathbf{t}(E)e^{-ikL}. \tag{1.1}$$

With this definition of the transmission coefficient, we no longer generate the traversal time, instead we measure the

additional time it takes to cross an atomic site due to the presence of an impurity, i.e., the *switching time*, $\mathcal{T}(E)$, through the impurity.

II. TIGHT-BINDING MODEL

In the TBA, it is assumed that atomic orbitals are highly localized, so that there is little overlap with the other atomic sites in the chain. We generate the Hamiltonian for the chain from the isolated orbital wave functions, $|s_n\rangle$, and invoke the nearest-neighbor approximation, so that

$$\mathbb{H} = \sum_{n=-\infty}^{\infty} [\alpha_n|s_n\rangle\langle s_n| + \beta_n(|s_n\rangle\langle s_{n+1}| + |s_{n+1}\rangle\langle s_n|)], \tag{2.1}$$

where the α_n (β_n) is the *Coulomb* (*resonance*) integral at (to) the nth site. In the unperturbed metal chain, $\alpha_n = \alpha$ and $\beta_n = \beta$, for all n.

For an energy eigenstate of the chain, $\mathbb{H}|\Phi(E)\rangle = E|\Phi(E)\rangle$, we expand the wave function as a superposition of atomic-orbital wave functions,

$$|\Phi(E)\rangle = \sum_{n=-\infty}^{\infty} c_n(E)|s_n\rangle, \tag{2.2}$$

which leads to the difference equation

$$qc_n = c_{m-1} + c_{m+1}, \tag{2.3}$$

where $q = (E - \alpha)/\beta$ is the *reduced energy*.

Knowing how a wave function changes between any two sites is sufficient, along with the properties of the chain, to define the wave function everywhere via

$$\mathbf{R}_m = \mathbf{P}^{m-n}\mathbf{R}_n, \tag{2.4}$$

where

$$\mathbf{R}_n = \begin{bmatrix} c_n \\ c_{n-1} \end{bmatrix} \quad \text{and} \quad \mathbf{P} = \begin{bmatrix} q & -1 \\ 1 & 0 \end{bmatrix} \tag{2.5}$$

are the *site vector* and the *propagation matrix*, respectively.

The eigenvalues of $\mathbf{P}$ are given by $\lambda_{\pm} = (1/2)(q \pm \sqrt{q^2 - 4})$ or, upon setting $q = 2\cos\theta$, by $\lambda_{\pm} = e^{\pm i\theta}$, which allows us to diagonalize the system, using the *unimodular* matrix,

$$\mathbf{U} = \frac{1}{\sqrt{2i\sin\theta}} \begin{bmatrix} e^{i\theta} & e^{-i\theta} \\ 1 & 1 \end{bmatrix}, \qquad (2.6)$$

by defining site vectors $\mathbf{V}_n = \mathbf{U}^{-1}\mathbf{R}_n$ and the diagonal propagation matrix $\mathbf{D} = \mathbf{U}^{-1}\mathbf{P}\mathbf{U}$. Substituting these into (2.4) yields

$$\mathbf{V}_n = \mathbf{D}^{n-m}\mathbf{V}_m. \qquad (2.7)$$

The eigenfunctions of the system are Bloch waves, whence

$$\mathbf{V}_n = \begin{bmatrix} v_n \\ w_n \end{bmatrix} = \begin{bmatrix} e^{in\theta} \\ e^{-in\theta} \end{bmatrix}, \qquad (2.8)$$

which characterizes the wave function by its right- (left-) moving component v_n (w_n).

Introducing an impurity at the origin, we can compress the perturbation into a δ-function potential,[10] so that the transfer matrix $\mathbf{T}(E)$, is given by

$$\mathbf{V}_{0^+} = \mathbf{T}(E)\mathbf{V}_{0^-}, \qquad (2.9)$$

which means that (2.7) now contains a discontinuity, namely,

$$\mathbf{V}_n = \begin{cases} \mathbf{D}^n \mathbf{V}_{0^-}, & n < 0, \\ \mathbf{D}^n \mathbf{V}_{0^+}, & n > 0. \end{cases} \qquad (2.10)$$

III. SWITCHING TIME

Adapting the method of ML (Ref. 7) to the TBA, we consider a wave function constructed from two Bloch waves with different energies to be incident from the left upon the impurity site at the origin. Although there will be both reflected and transmitted waves, we are interested only in those moving to the right, i.e., the v_n component of the wave function. We find

$$v_n = \begin{cases} e^{in\theta_E} + e^{in\theta_{(E+\Delta E)}}, & n < 0, \\ \mathbf{t}(E)e^{in\theta_E} + \mathbf{t}(E+\Delta E)e^{in\theta_{(E+\Delta E)}}, & n > 0, \end{cases} \qquad (3.1)$$

$\mathbf{t}(E)$ being the complex transmission coefficient (1.1).

Treating ΔE as a perturbation to E, we expand $\mathbf{t}(E)$ in a Taylor series,

$$\mathbf{t}(E + \Delta E) = \mathbf{t}(E) + \frac{\partial \mathbf{t}(E)}{\partial E}\Delta E + O(\Delta E^2), \qquad (3.2)$$

which we substitute back into (3.1) to give

$$v_n = \begin{cases} e^{in\theta_E} + e^{in\theta_{E+\Delta E}}, & n < 0, \\ \mathbf{t}(E)[e^{in\theta} + e^{in\theta_{(E+\Delta E)}}] + \dfrac{\partial \mathbf{t}(E)}{\partial E}\Delta E\, e^{in\theta_{(E+\Delta E)}} + O(\Delta E^2), & n > 0. \end{cases} \qquad (3.3)$$

The transmitted wave function will, therefore, replicate, up to a scale factor, the incident wave function, provided the first-order term remains subdominant. The transmitted wave will be affected nontrivially, through the transmission coefficient, when ΔE is such that

$$\frac{\partial \mathbf{t}(E)}{\partial E}\Delta E = O(\mathbf{t}(E)), \qquad (3.4)$$

which defines the associated characteristic time scale via the minimized *energy-time uncertainty relation*,

$$\Delta E\, \mathcal{T}(E) = \frac{\hbar}{2}. \qquad (3.5)$$

Combining (3.4) and (3.5), we obtain a time scale

$$\mathcal{T}(E) = \frac{\hbar}{2\Delta E} = O\left(\hbar \frac{1}{\mathbf{t}(E)}\frac{\partial \mathbf{t}(E)}{\partial E}\right) = O\left(\hbar \frac{\partial \ln \mathbf{t}(E)}{\partial E}\right), \qquad (3.6)$$

which describes the effects of the impurity. By evaluating (3.6) for systems for which the characteristic time is available by other methods (see the Appendix), we find that it is appropriate to use a scaling factor of unity. Thus, we write

$$\mathcal{T}(E) = \left| \frac{\hbar}{\mathbf{t}(E)} \frac{\partial \mathbf{t}(E)}{\partial E} \right|, \qquad (3.7)$$

which appears identical in form to the results of ML.[7] We stress, however, that the quantity measured in (3.7) is *not* the same as the ML derivation (see the Appendix), nor is it the time delay,[6] which accounts only for the imaginary part of (3.6).

IV. MOLECULAR SWITCH APPLICATION

The presence of an impurity state at the origin alters the atomic orbital wave function there. As obtained from (2.1), the Coulomb integral, $\langle s_0 | \mathbb{H} | s_0 \rangle$, and the two overlap integrals, $\langle s_{-1} | \mathbb{H} | s_0 \rangle$ and $\langle s_0 | \mathbb{H} | s_1 \rangle$, must be redefined. We set

$$\alpha_0 = \alpha', \quad \beta_{-1} = \gamma, \quad \beta_0 = \gamma' \qquad (4.1)$$

from which we define the *dimensionless* impurity parameters

$$X = \beta^{-1}(\alpha - \alpha'), \quad Y = \beta^{-1}\gamma,$$

$$Z = \gamma^{-1}\gamma', \quad W = 2^{-1/2}Y\sqrt{1 + Z^2}. \qquad (4.2)$$

As shown previously,[9,10] (2.3) for $n = -1, 0, 1$ gives the boundary conditions

$$qc_{-1}=c_{-2}+Yc_0,$$

$$(q-X)c_0=Yc_{-1}+YZc_1, \qquad (4.3)$$

$$qc_1=YZc_0+c_2,$$

which define unique propagation matrices across the sites affected by the impurity. Thus, we have

$$\mathbf{R}_2=\mathbf{P}_1\mathbf{P}_0\mathbf{P}_{-1}\mathbf{R}_{-1}. \qquad (4.4)$$

Multiplying (4.4) on the left by $\mathbf{D}^{-2}\mathbf{U}^{-1}$ and using identity matrices, (2.10) and the definitions of the site vectors, we obtain

$$\mathbf{V}_{0^+}=\mathbf{D}^{-2}\mathbf{U}^{-1}\mathbf{P}_1\mathbf{P}_0\mathbf{P}_{-1}\mathbf{U}\mathbf{D}^{-1}\mathbf{V}_{0^-}. \qquad (4.5)$$

Comparing (4.5) to (2.9) yields the elements of the transfer matrix $\mathbf{T}(E)$. Specifically, we have

$$T_{11}=\frac{1}{2}\left(Z+\frac{1}{Z}\right)+i\frac{[X+q(W^2-1)]}{ZY^2\sqrt{4-q^2}}, \qquad (4.6)$$

which has the well-known relation to the transmission coefficient, $T_{11}=1/\mathbf{t}^*$. In polar coordinates,

$$T_{11}=(\mathbf{t}^*(q))^{-1}=t^{-1/2}e^{i\phi}=t^{-1/2}(\cos\phi+i\sin\phi), \qquad (4.7)$$

from which we find

$$\phi=\tan^{-1}(\ \mathrm{Re}(T_{11})^{-1}\ \mathrm{Im}(T_{11})) \qquad (4.8)$$

and

$$t=|T_{11}|^{-2}=(\ \mathrm{Re}(T_{11})^2+\ \mathrm{Im}(T_{11})^2)^{-1}. \qquad (4.9)$$

The polar form of (3.7) is

$$\mathcal{T}(q)=\frac{\hbar}{\beta}\sqrt{\left(\frac{d\phi}{dq}\right)^2+\frac{1}{t}\left(\frac{dt^{1/2}}{dq}\right)^2}. \qquad (4.10)$$

Thus, we differentiate (4.8) and (4.9) subject to (4.6) to obtain the energy-dependent switching time via (4.10), i.e.,

$$\mathcal{T}(q)=\frac{\hbar}{|\beta|}\frac{|4(W^2-1)+qX|}{(4-q^2)\sqrt{W^4(4-q^2)+[X+q(W^2-1)]^2}}. \qquad (4.11)$$

Analysis of the impurity-embedded chain[9,10] has shown that the optimum transmission occurs when the impurity-bond ratio is symmetric, i.e., $Z=1$, and the energy of the impurity state coincides with the Fermi level, q_μ, i.e.,

$$(1-Y^2)^{-1}X=q_\mu. \qquad (4.12)$$

Setting $q_\mu=1$, and using the above optimization conditions in (4.11), we have

$$\mathcal{T}_{\mathrm{op}}(q)=\frac{\hbar}{|\beta|}\frac{(4-q)(1-Y^2)}{(4-q^2)\sqrt{Y^4(4-q^2)+(1-q)^2(1-Y^2)^2}}. \qquad (4.13)$$

From Fig. 1, we see that the switching time is relatively constant over most of the band, but rises rapidly at the band edges, where $\mathcal{T}(q)$ diverges. Once the impurity-chain bond ratio drops below 0.5, a significant delay develops at ener-
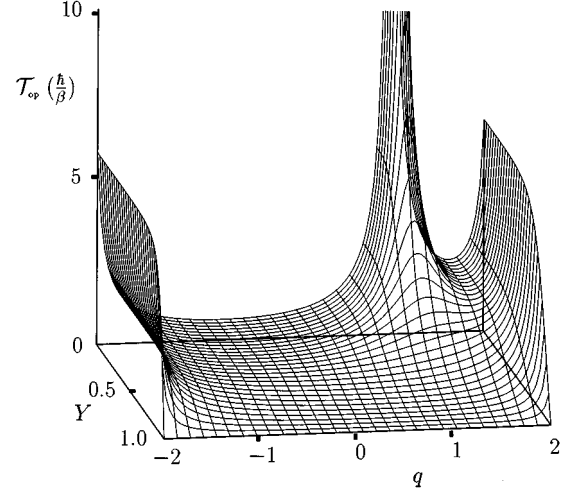

FIG. 1. Energy and impurity-bond dependence of switching time under optimized transmission conditions.

gies about the Fermi level. Since a low switching time is a desirable feature in a ''good'' molecular switch, the design of a practical device should avoid this region. As the majority of charge carriers transmitted by the switch have energies close to the Fermi level, avoiding the region means keeping $Y>0.5$.

The effects of the distribution of transmitted energies can be accounted for by convolution with the derivative of the Fermi-Dirac distribution, i.e., the *Azbel energy averaging*.[14,15] In this way, we obtain the characteristic time of the switch, as determined by the impurity parameters. It is, however, physically appropriate to obtain the average frequency with the Azbel method, instead of applying it directly to the switching time. Thus, we define the *effective switching time* using the reciprocal of $\mathcal{T}$, namely,

$$\frac{1}{\mathcal{T}_{\mathrm{eff}}}=\int_{\mathrm{band}}\frac{1}{\mathcal{T}(q)}\left[-\frac{\partial f(q)}{\partial q}\right]dq, \qquad (4.14)$$

where $f(q)$ is the Fermi-Dirac distribution,

$$f(q)=[1+\exp(\tau^{-1}(q-q_\mu))]^{-1}, \qquad (4.15)$$

τ being the reduced dimensionless temperature, $\beta^{-1}k_bT$. The results for optimal transmission at temperatures of $T=0$ K and $T=50$ K are shown in Fig. 2 for molecular systems with $\beta\sim1$ eV. With these assumptions in mind, the time scale in seconds is also provided. Again, for $Y<0.5$, we begin to see a significant increase in the time.

V. CONCLUSIONS

Using the tight-binding model, we have generated a characteristic time for transmission, derived from the ML energy-modulated traversal time. Unlike the traversal time, the switching time measures only the *delay* caused by tunnelling through an impurity at an atomic site, i.e., we have $\mathcal{T}=0$ for a pure chain that admits full transmission.

The information gathered from transfer-matrix analyses of molecular switches embedded in one-dimensional monatomic chains enables both the energy-dependent and effective switching times to written in terms of the impurity pa-
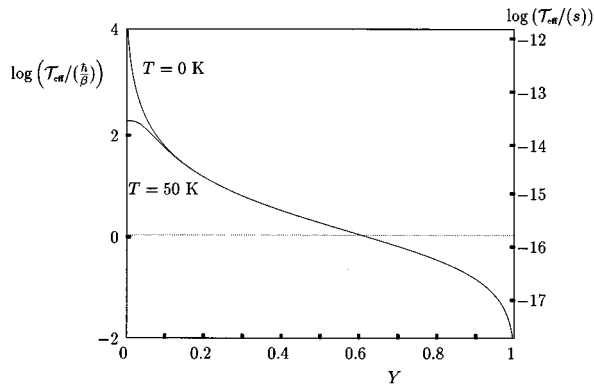
FIG. 2. log of energy-independent effective switching time as a function of impurity-chain bond ratio, subject to optimal transmission conditions. Curves are for temperatures $T=0$ K and $T=50$ K. For $\beta=1$ eV, the approximate time scale for seconds is provided.

rameters. The resulting equations show an inverse correlation between impurity-bond strength and switching time. Identifying low switching time as a desirable property of a ''good'' molecular switch leads to the preference for strong impurity-chain bonds, in contrast to the sharp-switching property favored by weak impurity-chain bonds.

APPENDIX: SCALE FACTOR FOR SWITCHING TIME

To show that unity is the appropriate scale factor in defining (3.7), we consider the unperturbed calculation. Since $\mathbf{t}(E)\equiv1$ in this case, $\mathcal{T}(E)=0$ and we obtain no information from the tight-binding situation. We therefore revert to the potential model and the traversal time, via (1.1), i.e., where we have $\mathbf{t}=e^{ikL}$ and $k=\sqrt{2mE}/\hbar$.

Evaluating the traversal time, we find

$$\tau=\left|i\hbar L\frac{\partial k}{\partial E}\right|=\frac{mL}{\hbar k}. \tag{A1}$$

Identifying $\hbar k/m$ with the classical velocity, we see that the traversal time requires the scale factor of unity to equate it with the transit time.

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