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Applied-field effects on molecular switches*

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Abstract. Electron transmission through an electrified composite metal-doped polymer–metal system is investigated by means of the Lippmann–Schwinger equation. The electric field, applied via the metal leads, acts across the polymer chain containing the single-impurity atom, which behaves as a molecular switch. The Stark-ladder effect in the doped polymer is described by utilizing the recursive-Green-function (RGF) approach, where repeated use of the Dyson equation gives rise to a continued-fraction form of the RGF, which can be expressed analytically as a ratio of Bessel functions. Molecular switch control of the transmission is achieved by adjusting the parameters characterizing the impurity. The influence of the applied field on the transmission process is discussed.

1. Introduction

The theoretical prediction [1] and experimental discovery [2] of *conducting polymers* in the seventies ushered in the era of *molecular electronics* in the realm of microelectronics. In developing molecular devices, a key component is the *molecular switch* (MS), for which several mechanisms are available [3]. For example, a hemiquinone molecule exhibits *two* forms that can be controlled by application of a potential field, perpendicular to the current direction, thus allowing the molecule to be switched from an *acceptor* state to a *donor* one [3, 4]. In another case, crystals of *tetra-cyanoquinodimethane* (TCNQ) derivatives complexed with metal *ions*, when subjected to a high voltage, were converted into TCNQ and metal *atoms*, in the course of which the system switched from a *high* to a *low* resistivity [3, 5]. *Photoswitches* have also aroused considerable interest. Taking a ‘leaf’ from biology, Shipman [6] studied molecules used in photosynthesis, while bacteriorhodopsin was investigated by Keszthelyi *et al* [7]. Carter proposed organic chromophores [3, 8], whose charges and double bonds alter when illuminated.

In essence, regardless of the switching mechanisms involved, they may be modelled via the change in the electronic configuration of a *single impurity* embedded in a conducting polymer. Within the *tight-binding* (TB) framework, the one-dimensional system . . . AAABAAA . . . represents an impurity B embedded in a periodic host chain of A atoms. Although the A atoms in reality have many orbitals, for the purpose of a qualitative view

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of the impurity effects, a single-orbital approach is adopted. A more detailed analysis of the system is required to ascertain the optimal *chemical* description of the impurity. Modification of the impurity's electronic configuration is achieved by changing its *site* or *bond* energies in the chain.

Sautet and Joachim [9] examined such a *metallic* chain with equal bonds, while English and Davison [10] investigated its *semiconductor* counterpart with alternating bonds. The scattering-matrix technique was employed in both studies to obtain the impurity transmission coefficient and the change in the density of states. Subsequently, Mišković *et al* treated a two-impurity system [11], then a one-impurity one [12] via the many-neighbour approximation [13], using the *Lippmann–Schwinger* (LS) [14] scattering equation in each case. Concomitantly, English *et al* [15] performed a TB study of the interaction time for MSs, based on the Martin–Landauer approach [16].

Initial interest in polymer-based devices was in the *field-effect transistor*, with the discovery in the late 1980s that the field effect could be routinely achieved in devices fabricated by the deposition of conjugated polymers onto insulator layers, such as silicon dioxide [17–20].

Field effects in solids have a long and venerable history, dating back to Zener's work on dielectric breakdown in the thirties [21]. Recently, the *Stark-ladder* (SL) effect in electrified TB systems has been investigated by Davison *et al* [22], who used the recursive-Green-function (RGF) method, which involves successive use of the Dyson equation. The RGFs were generated in the site representation, in the form of continued fractions, which were then expressed analytically as ratios of Bessel functions (BFs). The local density of states at the surface and in the bulk were obtained and their dependency on the applied electric field discussed. The RGF approach has also been employed to investigate the SL effect on surface states [23] and chemisorption [24].

We now turn to the question that we wish to address in this article, namely, 'How are the transmission properties of a MS affected by an applied field?' The system under examination has a *sandwich structure* consisting of two metal leads separated by a polymer containing a single impurity. The metal/polymer/metal (MPM) system is subjected to an electric field by applying a voltage across the polymer by means of the metal leads. The electronic structure of the MPM is described in terms of the TB method in which the wavefunction coefficients are obtained via the LS relation. The coefficients then provide access to the transmission coefficient of the impurity, which is related to the *transmission probability* by the transfer-matrix approach [9, 10]. The transmission probability can be controlled, through the manipulation of the impurity site parameters, thereby producing a MS. In some respects, the formulation adopted here reflects that used by Glick and co-workers [25], in their tunnelling studies of sandwich structures.

2. Zero-field treatment

Consider an *infinite* chain of atoms of site (bond) energy α (β). In *projection-operator* notation, its Hamiltonian is

$$\mathbb{H}^0 = \sum_{n=-\infty}^{\infty} [\alpha|n\rangle\langle n| + \beta(|n\rangle\langle n+1| + |n+1\rangle\langle n|)] \quad (2.1)$$

which has the well-known GF \mathbb{G}^0 , with the matrix elements [26]

$$G_{\infty}^0(n, m) \equiv \langle n|\mathbb{G}^0|m\rangle = \frac{i}{2\beta} \frac{e^{|n-m|\theta}}{\sin\theta}. \quad (2.2)$$

Here, $\theta = ka$ (k being the electron wavenumber and a the chain period), so the electron energy dispersion reads $E = \alpha + 2\beta \cos \theta$. On introducing a *localized perturbation*, \mathbb{V} , well away from the chain ends ($n \rightarrow \pm\infty$), equation (2.1) becomes the perturbed Hamiltonian

$$\mathbb{H} = \mathbb{H}^0 + \mathbb{V}. \quad (2.3)$$

The perturbed and unperturbed wavefunctions are connected via the LS equation [14]; that is,

$$|\psi\rangle = |\psi^0\rangle + \mathbb{G}^0 \mathbb{V} |\psi\rangle \quad (2.4)$$

which is the wavefunction equivalent of the *Dyson equation* [26]. Performing an atomic-orbital (AO) expansion of wavefunctions in (2.4) and multiplying on the left by $\langle n|$, we obtain

$$c_n = c_n^0 + \sum_{\ell, m} G^0(n, \ell) V(\ell, m) c_m \quad (2.5)$$

as the LS relation for the wavefunction coefficients, with $V(\ell, m) \equiv \langle \ell | \mathbb{V} | m \rangle$.

In the case of a *normalized* wave incident from the left, the AO wavefunction coefficients in (2.5) are given by

$$c_n = \begin{cases} e^{in\theta} + r e^{-in\theta} & n \rightarrow -\infty \\ \tau e^{in\theta} & n \rightarrow \infty \end{cases} \quad (2.6)$$

where r (τ) is the *reflection* (*transmission*) coefficient. For propagation through the crystal, the plane waves are replaced by *Bloch waves* by setting $\theta = ka$ and $x = na$.

Restricting the scattering potential to the vicinity of the origin, i.e., $V(\ell, m) = 0$, when either $|\ell| > N$ or $|m| > N$ for some finite N , we apply (2.2) to (2.5) as $n \rightarrow -\infty$, whereby

$$c_n \rightarrow e^{in\theta} + \sum_{\ell, m} \frac{i}{2\beta \sin \theta} e^{i(\ell-n)\theta} V(\ell, m) c_m. \quad (2.7)$$

Comparing (2.7) with (2.6), we have

$$r = \frac{i}{2\beta \sin \theta} \sum_{\ell, m} e^{i\ell\theta} V(\ell, m) c_m. \quad (2.8)$$

Similarly, taking $n \rightarrow \infty$, equations (2.5) and (2.6) lead to

$$\tau = 1 + \frac{i}{2\beta \sin \theta} \sum_{\ell, m} e^{-i\ell\theta} V(\ell, m) c_m. \quad (2.9)$$

We now model a MS by placing the *impurity atom* at the origin (site 0) [9, 10] and parametrize its site energy as α_s and the energies of the bonds to the neighbouring sites -1 and 1 as ρ_- and ρ_+ , respectively. The corresponding perturbation potential operator is

$$\mathbb{V} = \beta [2z_s |0\rangle \langle 0| + (\sigma - 1) | -1\rangle \langle 0| + |0\rangle \langle -1| + (\sigma y - 1) (|0\rangle \langle 1| + |1\rangle \langle 0|)] \quad (2.10)$$

where

$$\sigma = \rho_- / \beta \quad y = \rho_+ / \rho_- \quad z_s = (\alpha_s - \alpha) / 2\beta \quad (2.11)$$

are *dimensionless reduced impurity parameters*. Applying (2.10) to (2.9) yields

$$\tau = 1 + A c_{-1} + (A e^{i\theta} + B + e^{-i\theta} C) c_0 + C c_1 \quad (2.12)$$

where

$$A = \frac{i(\sigma - 1)}{2 \sin \theta} \quad B = \frac{i z_s}{\sin \theta} \quad C = \frac{i(\sigma y - 1)}{2 \sin \theta}. \quad (2.13)$$

Solution of (2.12) requires equations for c_{-1} , c_0 and c_1 , which are obtained from (2.2), (2.5) and (2.10) by setting $n = -1, 0$ and 1 . The solutions to these equations are

$$c_{-1} = [(2e^{2i\theta} - 1 - e^{4i\theta})C^2 + 2e^{i\theta}(e^{2i\theta} - 1)C - (1 - e^{2i\theta})B + 1]/\Delta \quad (2.14)$$

$$c_0 = [(1 - e^{2i\theta})A + e^{i\theta}]/\Delta \quad (2.15)$$

$$c_1 = [(1 - e^{2i\theta})C + e^{i\theta}][(1 - e^{2i\theta})A + e^{i\theta}]/\Delta \quad (2.16)$$

where

$$\Delta = e^{i\theta}[(e^{2i\theta} - 1)(A^2 + C^2) - 2e^{i\theta}(A + C) + 1 - B]. \quad (2.17)$$

Thus, inserting (2.14) to (2.17) into (2.12) and using (2.13), we arrive at

$$\tau = \sigma^2 y \left\{ \omega^2 - i[z_s + X(\omega^2 - 1)](1 - X^2)^{-1/2} \right\}^{-1} \quad (2.18)$$

where

$$\omega = \sigma \left[(1 + y^2)/2 \right]^{1/2} \quad (2.19)$$

and $X = (E - \alpha)/(2\beta)$ is the *reduced energy*. Note that, for electron energies inside the band, $-1 \leq X \leq 1$, we have used the relation $\exp(i\theta) = X + i\sqrt{1 - X^2}$ in deriving (2.18).

The *transmission probability* is given by

$$\mathcal{T}(X) = |\tau|^2 = 4(y + y^{-1})^{-2} \left\{ 1 + \frac{[z_s + X(\omega^2 - 1)]^2}{\omega^4(1 - X^2)} \right\}^{-1} \quad (2.20)$$

which is in accord with the transfer-matrix result [9, 10]. Implementing Azbel's *energy-independent* technique [27], one may integrate (2.20) over the energy band, but weighted by the energy derivative of the *Fermi-Dirac distribution* $f(E, E_f, k_b T)$, E_f being the Fermi energy, T the absolute temperature and k_b the Boltzmann constant. We shall consider the *temperature-independent limit*, $k_b T \ll \beta$, so the *effective-transmission probability* t_{eff} reduces to

$$t_{eff} = \mathcal{T}(X_f) \quad (2.21)$$

where X_f is the reduced Fermi energy.

3. Electrified polymer sandwich

We now focus our attention on the MPM-sandwich structure, where the *finite* P chain lies between the sites $n = 0$ and N , and *semi-infinite* M leads are connected to the P ends by bonds of energy δ (figure 1). An *electric field* of gradient Γ , applied to the P chain, gives rise to a *potential difference*, $\phi = N\Gamma$, between the *M-lead* sites at $n = -1$ and $N + 1$. The bond energies in both the leads are β , while the site energies are α and γ ($=\alpha + \phi$) in the left-hand and right-hand leads, respectively. The presence of the linear field across the P chain perturbs each site energy [22], so at the n -atom, $\alpha'_n = \alpha' + n\Gamma$. Meanwhile, throughout the chain, the bond energy is β' .

As in the chemisorption situation [24], the field strength must be such as to ensure that *ionization* of the P chain is *avoided*. Consequently, we require the restraint that $|N\Gamma/2\beta'| < 2$, which allows at least *one* state to remain *delocalized* across the field region of the P chain. In fact, for *ideal* transmission through the chain, a state must remain delocalized across the *entire* MPM system. Specifically, the allowed energy bands in the M leads must *overlap*, whence, $|\phi| < |4\beta|$.

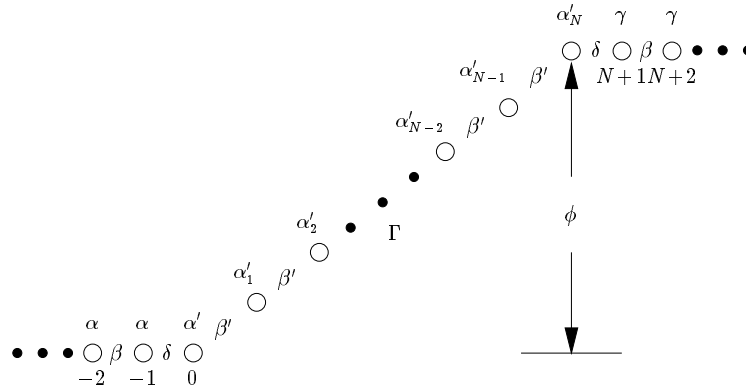


Figure 1. A diagram showing an electrified MPM sandwich. The left-hand (right-hand) semi-infinite metal lead occupies the region $n \leq -1$ ($n \geq N + 1$) with site and bond energies α and β (γ and β). The polymer lying in the Γ -field region $0 \leq n \leq N$ has site (bond) energy α'_n (β'), where $\alpha'_n = \alpha + n\Gamma$ and $\phi = N\Gamma$ is the potential difference between M leads connected to the P chain by δ -bonds.

The *reduced energy* in the *right-hand lead* is defined by [26]

$$X' = (E - \alpha - \phi)/2\beta = X - U = \cos w \tag{3.1}$$

where

$$U = \phi/2\beta \tag{3.2}$$

is the *reduced potential difference* and $w = k'a$ (k' being the electron wavenumber in the right-hand lead). Thus, the *band overlap* is defined by $U - 1 < X < 1$.

In order to use the LS equation, we treat the *unperturbed* system as consisting of three *isolated* portions, the left-hand semi-infinite M lead, the finite electrified P chain, and the right-hand semi-infinite M lead. A *right-moving* Bloch wave is introduced at $n = -\infty$. Since the energy references in the two M leads are different, care must be taken in normalizing the Bloch waves. The required condition is that the *local probability current* must be *constant* throughout the MPM system.

Following Caroli *et al* [28], the *probability-current operator* is defined to be proportional to the *projected difference* between adjacent sites; that is,

$$\mathbb{J}_n = J(|n + 1\rangle\langle n| - |n\rangle\langle n + 1|) \tag{3.3}$$

whose expectation value is

$$\langle \psi | \mathbb{J}_n | \psi \rangle = J(c_{n+1}^* c_n - c_n^* c_{n+1}). \tag{3.4}$$

Hence, an *incoming* Bloch wave, $c_n = \mathcal{A}e^{in\theta}$, in the *left-hand lead* will have a *probability current*

$$J_{-\infty} = J\mathcal{A}^2(e^{-i\theta} - e^{i\theta}) = -2iJ\mathcal{A}^2 \sin \theta \tag{3.5}$$

while, for the *outgoing* wave, $c_n = \mathcal{B}e^{inw}$, in the *right-hand lead*, we have

$$J_{\infty} = J\mathcal{B}^2(e^{-iw} - e^{iw}) = -2iJ\mathcal{B}^2 \sin w. \tag{3.6}$$

Requiring (3.5) to equal (3.6) leads to the *energy-independent solution* in which

$$\mathcal{A} = (\sin \theta)^{-1/2} \quad \mathcal{B} = (\sin w)^{-1/2}. \tag{3.7}$$

Thus, equation (2.6) gives

$$c_n = \begin{cases} (\sin \theta)^{-1/2} e^{in\theta} + r(\sin \theta)^{-1/2} e^{-in\theta} & n \rightarrow -\infty \\ \tau(\sin w)^{-1/2} e^{in\theta} & n \rightarrow \infty. \end{cases} \quad (3.8)$$

The coefficients, c_n^0 , for the *left-hand* semi-infinite lead are obtained from the infinite system by using the *bond-breaking* operator

$$\mathbb{V} = -\beta \left(| -1 \rangle \langle 0 | + | 0 \rangle \langle -1 | \right) \quad (3.9)$$

in the LS equation (2.5), which yields

$$c_n^0 = (\sin \theta)^{-1/2} e^{in\theta} - \beta \left[G_\infty^0(n, -1) c_0^0 + G_\infty^0(n, 0) c_{-1}^0 \right]. \quad (3.10)$$

The coefficients c_0^0 and c_{-1}^0 are readily eliminated by utilizing (3.10) with $n = 0$ and $n = -1$, so, by dint of (2.2), equation (3.10) yields

$$c_n^0 = (\sin \theta)^{-1/2} (e^{in\theta} - e^{in|\theta|}) = \begin{cases} 2i(\sin \theta)^{-1/2} \sin n\theta & n \leq -1 \\ 0 & n \geq 0. \end{cases} \quad (3.11)$$

The GFs for the M leads are derived from the infinite chains, by means of the *bond-cleaving* potential operator

$$\mathbb{V} = -\beta \left(| -1 \rangle \langle 0 | + | 0 \rangle \langle -1 | + | N \rangle \langle N + 1 | + | N + 1 \rangle \langle N | \right) \quad (3.12)$$

which in Dyson's equation (cf. (2.4)) leads to

$$G(n, m) = G_\infty^0(n, m) - \beta \left[G_\infty^0(n, -1) G(0, m) + G_\infty^0(n, 0) G(-1, m) \right. \\ \left. + G_\infty^0(n, N) G(N + 1, m) + G_\infty^0(n, N + 1) G(N, m) \right] \quad (3.13)$$

for the semi-infinite M-lead GFs.

In the *left-hand* lead, where $n, m \leq -1$ and $X = \cos \theta$, we note that $G(n, m) = 0$, whenever n or m lie *outside* that lead. Thus, (3.13) yields

$$\beta G(n^-, m^-) = -(2i \sin \theta)^{-1} [e^{i|n-m|\theta} - e^{i|n|\theta}] \beta G(-1, m) \quad (3.14)$$

by (2.2). For $n^- = -1$, equation (3.14) provides

$$\beta G(-1, m) = e^{i|m+1|\theta} e^{i\theta} \quad (3.15)$$

which in (3.14) gives

$$\beta G(n^-, m^-) = (2i \sin \theta)^{-1} (e^{i|n|\theta} e^{i|m+1|\theta} e^{i\theta} - e^{i|n-m|\theta}). \quad (3.16)$$

In particular, on setting $m = -1$, we have

$$\beta G(n^-, -1) = e^{-in\theta}. \quad (3.17)$$

Likewise, for the *right-hand* lead, $n, m \geq N + 1$ and $X' = \cos w$, and by analogy with (3.14), we see that

$$\beta G(n^+, m^+) = -(2i \sin w)^{-1} [e^{i|n-m|w} - e^{i|n-N|w}] \beta G(N + 1, m) \quad (3.18)$$

where, again, $G(n, m) = 0$, for n or m outside the lead. For $n = N + 1$, equation (3.18) reduces to

$$\beta G(N + 1, m) = e^{i|m-N-1|w} e^{iw}. \quad (3.19)$$

Inserting (3.19) in (3.18), we arrive at

$$\beta G(n^+, m^+) = (2i \sin w)^{-1} (e^{i|n-N|w} e^{i|m-N-1|w} e^{iw} - e^{i|n-m|w}) \quad (3.20)$$

i.e., when $m = N + 1$,

$$\beta G(n^+, N + 1) = e^{i(n-N)w}. \tag{3.21}$$

Having obtained the M leads' components, we connect them to the *finite P chain*, whose Greenian is G_{0N} , by means of (3.12) with $-\beta$ replaced by δ , and the *unperturbed* GFs

$$G^0(n, m) = \begin{cases} G_{-1^-}(n, m) & n, m \leq -1 \\ G_{0N}(n, m) & 0 \leq n, m \leq N \\ G_{(N+1)^+}(n, m) & n, m \geq N + 1 \\ 0 & \text{otherwise.} \end{cases} \tag{3.22}$$

In the case of the *left-hand* lead, where $n \leq -1$, the LS equation (2.5) with the δ -version of (3.12) reads

$$c_{n^-} = c_n^0 + \delta G^0(n, -1)c_0 = 2i(\sin \theta)^{-1/2} \sin n\theta + \lambda e^{-in\theta} c_0 \quad \lambda = \delta/\beta \tag{3.23}$$

via (3.11) and (3.17), with $\lambda = \delta/\beta$ being the *reduced bond energy* between the P chain and the M leads. In particular, equation (3.23) gives

$$c_{-1} = -2i(\sin \theta)^{1/2} + \lambda e^{i\theta} c_0. \tag{3.24}$$

Inside the *P chain*, the LS equation (2.5) leads to

$$c_0 = \delta [G_{0N}(0, 0)c_{-1} + G_{0N}(0, N)c_{N+1}] \tag{3.25}$$

$$c_N = \delta [G_{0N}(N, 0)c_{-1} + G_{0N}(N, N)c_{N+1}]. \tag{3.26}$$

Similarly, for the *right-hand* lead $m \geq N + 1$, and we find

$$c_m = \delta G^0(m, N + 1)c_N = \lambda e^{i(m-N)w} c_N \tag{3.27}$$

via (2.5), (3.12) and (3.21), whence

$$c_{N+1} = \lambda e^{iw} c_N. \tag{3.28}$$

After some manipulation, equation (3.25) in (3.24) provides the implicit solution

$$c_{-1} = \frac{-2i(\sin \theta)^{1/2} + \lambda^2 e^{i\theta} \beta G_{0N}(0, N)}{1 - \lambda^2 e^{i\theta} \beta G_{0N}(0, 0)} c_{N+1}. \tag{3.29}$$

Using (3.28) and (3.29), we can write (3.26) as

$$c_N = -2i(\sin \theta)^{1/2} \lambda \beta G_{0N}(N, 0) / D \tag{3.30}$$

where

$$D = [1 - \lambda^2 \beta G_{0N}(0, 0)e^{i\theta}] [1 - \lambda^2 \beta G_{0N}(N, N)e^{iw}] - \lambda^4 e^{i(\theta+w)} \beta^2 G_{0N}^2(0, N) \tag{3.31}$$

with $G_{0N}(0, N) = G_{0N}(N, 0)$. We note here that, inside the band-overlap region, one may use the relations

$$\exp(i\theta) = X + i\sqrt{1 - X^2}$$

and

$$\exp(iw) = X' + i\sqrt{1 - (X')^2} = X - U + i\sqrt{1 - (X - U)^2}$$

to express D in terms of the reduced energy X in the left-hand lead.

On equating (3.8) and (3.27), we find that the *transmission coefficient* is

$$\tau = \lambda(\sin w)^{1/2} e^{-iNw} c_N \tag{3.32}$$

which by (3.30), together with (2.19), (2.20) and (3.1), yields

$$\mathcal{T} = 4\lambda^2 \sqrt{1 - X^2} \sqrt{1 - (X - U)^2} \frac{|\beta G_{0N}(N, 0)|^2}{|D(X)|^2} \tag{3.33}$$

for the *transmission probability*.

Thus, the problem is now reduced to one of finding the GF elements, $G_{0N}(0, N)$, in the *finite* electrified P-chain region, which are available from previous studies [22, 24], namely,

$$\beta' G_{0,N}(0, N) = \prod_{n=0}^N \beta' G_{0,N}(n, n) \tag{3.34}$$

where

$$\beta' G_{0,N}(n, n) = - \frac{J_{v+n+N}(x)Y_{v+n}(x) - J_{v+n}(x)Y_{v+n+N}(x)}{J_{v+n-1}(x)Y_{v+n+N}(x) - J_{v+n+N}(x)Y_{v+n-1}(x)} \tag{3.35}$$

with J_μ (Y_μ) being a BF of the first (second) kind of order μ . Here,

$$x = -\eta N/U \quad v = -N(X - z)/U \tag{3.36}$$

with $\eta = \beta'/\beta$ and $z = (\alpha' - \alpha)/\beta$ being the *reduced* bond and site energies, respectively, of the P chain.

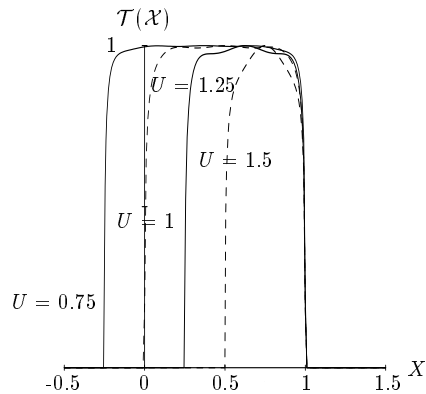


Figure 2. Band-overlap regions versus the electron energy $X = (E - \alpha)/(2\beta)$ in the left-hand lead for the potential differences $U = \phi/(2\beta)$ indicated.

As far as the transmission probability (3.33) is concerned, if the band structure of the electrified P chain is taken to be the *same* as that in the M leads, i.e., $\eta = 1$ and $z = 0$, then ramping the potential difference, U , *narrows* the *band-overlap* region (figure 2). For $U = 1$, the width of the overlap region is half that of the conduction band in the left-hand lead ($0 \leq X \leq 1$), so $N/2$ of the discrete states of the P chain are *embedded* in the overlap region. On varying the interface reduced bond strength, $\lambda = \delta/\beta$, figure 3(a) shows that, as it increases, the separation between the states spreads, while the states themselves broaden and increase in intensity until full transmission is attained at $\lambda = 1$, after which they become narrower and drop in intensity, while continuing to separate.

In the case where the P-chain and M-lead band structures *differ*, adjusting the reduced site energy of the P chain, z , will *rigidly shift* the embedded P field states *behind* the *overlap window*. Changing the reduced bond energy of the P chain, η , modifies the bandwidth of the P field region. For $\eta = 0.75$ and $z = -0.25$ (figure 3(b)), the states are shifted downward, leaving little transmission at the higher energies. The separation between P field states is

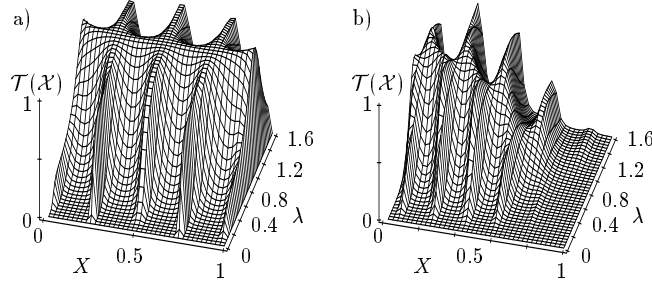


Figure 3. The transmission probability of embedded field states versus the electron energy $X = (E - \alpha)/(2\beta)$ in the left-hand lead and the interface bond strength $\lambda = \delta/\beta$ with the potential difference $U = \phi/(2\beta) = 1$. The reduced site and bond energies of the P chain, $z = (\alpha' - \alpha)/\beta$ and $\eta = \beta'/\beta$, are chosen so as to have: (a) identical band structure, $z = 0$, $\eta = 1$; (b) different band structure, $z = -0.25$, $\eta = 0.75$, compared to the M leads.

narrowed and the states themselves are reduced for low λ -values, but are sharpened when $\lambda > 1$.

4. Single-impurity switch

At this juncture, we introduce a *single-impurity atom* into the electrified P chain, and investigate the possibility of using it as a means of securing control of the transmission probability. As before, equation (2.11) defines the parameters describing the impurity, which is now located at the site M ($1 \leq M \leq N - 1$). Since (3.33) with (3.31) requires only the GFs involving the end sites of the P chain, we only need to construct a finite chain with an embedded impurity in a linear potential, by attaching finite chains to either side of the site- M impurity. Thus, the *unperturbed* GF is in three parts, i.e.,

$$G^0(n, m) = \begin{cases} G_{0, M-1}^0(n, m) & 0 \leq n, m \leq M - 1 \\ G_{M, M}^0(M, M) & n = m = M \\ G_{M+1, N}^0(n, m) & M + 1 \leq n, m \leq N \\ 0 & \text{otherwise} \end{cases} \quad (4.1)$$

which are *connected* via the potential operator

$$\mathbb{V} = \rho_- (|M - 1\rangle\langle M| + |M\rangle\langle M - 1|) + \rho_+ (|M\rangle\langle M + 1| + |M + 1\rangle\langle M|). \quad (4.2)$$

Invoking Dyson's equation (cf. (2.4)), we have

$$G_{0N}(0, 0) = G^0(0, 0) + \rho_- G^0(0, M - 1)G_{0N}(M, 0) \quad (4.3)$$

in which

$$G_{0N}(M, 0) = G_{0N}(0, M) = \rho_- G^0(0, M - 1)G_{0N}(M, M). \quad (4.4)$$

The on-site GF at the impurity is given by

$$G_{0N}(M, M) = G^0(M, M)[1 + \rho_- G_{0N}(M - 1, M) + \rho_+ G_{0N}(M + 1, M)] \quad (4.5)$$

where

$$G_{0N}(M \pm 1, M) = \rho_{\pm} G^0(M \pm 1, M \pm 1)G_{0N}(M, M). \quad (4.6)$$

Inserting (4.6) in (4.5) and rearranging generates the implicit equation

$$G_{0N}(M, M) = \left\{ G^0(M, M)^{-1} - [\rho_-^2 G^0(M-1, M-1) + \rho_+^2 G^0(M+1, M+1)] \right\}^{-1}. \quad (4.7)$$

Returning to (4.3), and using (4.4) and (4.7), we obtain

$$G_{0N}(0, 0) = G^0(0, 0) + \rho_-^2 G^0(0, M-1)^2 \times \left\{ G^0(M, M)^{-1} - [\rho_-^2 G^0(M-1, M-1) + \rho_+^2 G^0(M+1, M+1)] \right\}^{-1}. \quad (4.8)$$

Similarly, we have

$$G_{0N}(N, N) = G^0(N, N) + \rho_+ G^0(N, M+1) G_{0N}(M, N) \quad (4.9)$$

and

$$G_{0N}(M, N) = G_{0N}(N, M) = \rho_+ G^0(N, M+1) G_{0N}(M, M) \quad (4.10)$$

which, by (4.7), yield

$$G_{0N}(N, N) = G^0(N, N) + \rho_+^2 G^0(N, M+1)^2 \times \left\{ G^0(M, M)^{-1} - [\rho_-^2 G^0(M-1, M-1) + \rho_+^2 G^0(M+1, M+1)] \right\}^{-1}. \quad (4.11)$$

With the aid of (4.10) and (4.7), the cross-terms involving the end sites are provided by

$$G_{0N}(0, N) = G_{0N}(N, 0) = \rho_- G^0(0, M-1) G_{0N}(M, N) = \frac{\rho_- \rho_+ G^0(0, M-1) G^0(N, M+1)}{G^0(M, M)^{-1} - \rho_-^2 G^0(M-1, M-1) - \rho_+^2 G^0(M+1, M+1)}. \quad (4.12)$$

Finally, we use the impurity parameters in (2.10) at the site M to show that

$$G^0(M, M)^{-1} = 2\beta(X - z_s - MU/N). \quad (4.13)$$

Equations (4.8) and (4.11) to (4.13) enable (3.33) to be expressed in terms of the *known* GFs of the electrified P chain with an M -site impurity, whence, the influence of the applied field enters the transmission probability via the BF expression (3.35).

Employing (2.21), we choose the reduced impurity site energy $z_s = (\alpha_s - \alpha)/(2\beta)$ and the asymmetry of the impurity bonds to the host chain $y = \rho_+/\rho_-$, equation (2.11), as the candidates for describing the parameter space over which we wish to control the impurity [9, 10]. We adopt the system depicted in figure 3(b) with the interface reduced bond strength $\lambda = 0.75$. Taking the Fermi energy such that $X_f = 0.25$ and the reduced impurity bond to the host chain $\sigma = 0.8$, equation (2.11), we first set $y = 0.5$ and consider the effect of ramping the field via the reduced potential difference $U = \phi/(2\beta)$ on the z_s -curve (figure 4(a)). As U increases, the transmission peak increases in height to a resonance at $U = 0.25$, before decreasing again. In figure 4(b), we examine the case of $z_s = X_f = 0.25$, and treat y as the switching parameter. The peak transmission probability increases both in height and y -location, as U increases and doubles in value from $U = 0$ to 1. Comparison of the curves in figure 4 clearly shows that figure 4(a) has the desired feature of narrow maxima, required for good switching performance. Thus, z_s is the *preferred* switching parameter.

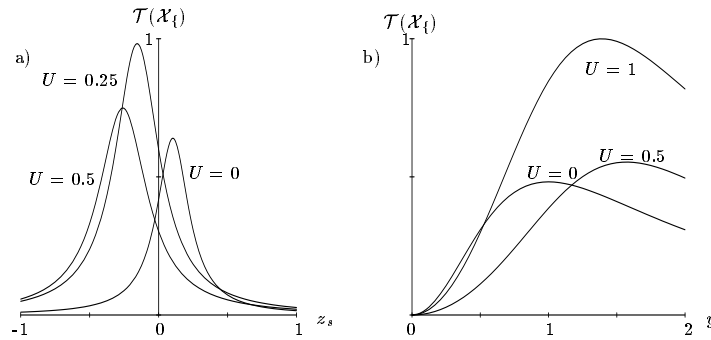


Figure 4. Transmission properties of a molecular switch at the Fermi energy $X = X_f = 0.25$ in terms of the impurity site energy $z_s = (\alpha_s - \alpha)/(2\beta)$ and the asymmetry of its bonds to the P chain $y = \rho_+/\rho_-$, for the potential differences $U = \phi/(2\beta)$ shown. The impurity bond to the host chain is $\sigma = \rho_-/\beta = 0.8$, the site and bond energies of the P chain are $z = (\alpha' - \alpha)/\beta = -0.25$ and $\eta = \beta'/\beta = 0.75$, while the interface bond strength is $\lambda = 0.75$. (a) $y = 0.5$ and z_s variable, (b) $z_s = 0.25$ and y variable.

5. Conclusion

The LS scattering equation has been invoked to study the electronic transmission of an electrified MPM sandwich, where the P chain contains an impurity switch. The applied voltage bias manifests itself by generating a SL energy spectrum in the doped P chain, which is analysed via the Dyson-equation approach. The RGF so obtained is expressed analytically in terms of BFs. Utilizing the RGF in the LS equation enabled expressions for the wavefunction coefficients to be derived, from which the transmission probability, $T(X)$, was found in terms of the reduced field, U , and impurity parameters (z_s, y). Plots of $T(X)$ in the (z_s, y) parameter space revealed z_s to be the more suitable switching parameter, while the presence of the field assisted the charge transport to a considerable extent.

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