An expression for the bridge-mediated electron transfer rate in dye-sensitized solar cells

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We have derived an expression for the rate of electron transfer between a semiconductor and a redox centre connected to the semiconductor via a molecular bridge. This model is particularly useful to study the charge recombination (CR) process in dye-sensitized solar cells, where the dye is often connected to the semiconductor by a conjugated bridge. This formalism, designed to be coupled with density functional theory electronic structure calculations, can be used to explore the effect of changing the bridge on the rate of interfacial electron transfer. As an example, we have evaluated the CR rate for a series of systems that differ in the bridge length.

1. Introduction

Dye-sensitized solar cells (DSSCs) may become an economically viable alternative to commercial solar cells based on different architectures if their efficiency can be increased beyond what is currently achievable [1]. The innovative element in DSSCs is the photoactive electrode, made of sintered nanoparticles of semiconducting material, TiO\textsubscript{2} in the original formulation [2]. These nanoparticles are in contact with an electrolyte solution and are sensitized to visible light by the adsorption of a dye, either an inorganic complex or an organic molecule [3–5]. Upon light irradiation, the molecule is promoted to an excited state and injects an electron into the TiO\textsubscript{2} conduction band, generating a photocurrent. An unwanted loss is caused by the charge recombination (CR) reaction, when the dye cation resulting from the charge injection (CI) process is neutralized by an electron in the semiconductor conduction band [6].
Many organic dyes are composed of a light-harvesting unit (a chromophore) connected to the TiO$_2$ surface via a molecular bridge terminated with an anchoring group [7]. The coupling between the chromophore and the semiconductor is mediated by the bridge fragment, and these systems can be considered analogous to the molecular donor–bridge–acceptor (DBA) systems studied in the photochemistry literature [8]. In this paper, we express the rate of CI and CR for chromophores connected to the semiconductor through a bridge by combining the theories developed to study DBA systems with the theories of electrochemical reactions and transport in molecular junctions.

The optimization of a DSSC is a very challenging task: the modification of one material within the device is bound to impact upon different microscopic processes taking place [9]. For this reason, the only systematic pathway towards more efficient cells is the separate optimization of the devices’ individual components. This approach has been gaining momentum recently, with studies focused, for example, on the dye’s anchoring group [10,11], where a computational study has been performed to predict the relative stability of the attachment and the efficiency of charge transfer across these anchors [12]. The design of new synthetic procedures for TiO$_2$ nanoparticles exposing different crystallographic faces [13] has added another tool for the engineering of interfacial electron transfer, with the CI process being noticeably affected by surface morphology [14–16]. In this respect, being able to express the rate for the interfacial charge-transfer process solely in terms of the properties of the dye, the bridge, the anchoring group and the interaction between these with the semiconductor surface is potentially very beneficial.

The bridge between the light-harvesting component of the dye and the semiconductor is one of the parameters that can potentially be optimized. In DBA systems, extensive studies have been carried out on the possibility of using different bridges to modulate the charge-transfer rate by changing the length of the bridge or the positions of its orbital levels [17–19]. Another parameter that can be controlled is the coupling between the bridge and the dye orbitals. We have recently shown that, by considering dyes of particular symmetry, it is possible to design a semiconductor–bridge–dye system with an extremely low rate of CR [20]. In DSSC, the CI rate is the fastest process, occurring with quantum efficiency close to one. A linear bridge typically controls both the CI and the CR rates. Being able to systematically reduce the two rates can be beneficial for the solar cell as long as the quantum efficiency of CI remains very high. With a slower CR, the efficiency of the cell can increase, because the loss channel of CR is less active [21,22], and a larger open-circuit voltage can be obtained [23], allowing the use of a redox mediator with more negative electrochemical potential to regenerate the longer-lived dye cation.

In this paper, we present the theory of CR mediated by a bridge. Several theoretical approaches have been developed for the related problem of transmission through a molecular bridge [24,25]; these include spin-boson models [26], quantum dynamics [27,28], scattering formalism [29,30] and Löwdin partitioning techniques [31]. The latter is similar, in principle, to the approach presented herein; however, the application to DSSCs has not been previously investigated. The theory will first be presented for a model Hamiltonian and then be generalized for a system whose parameters are obtained from an electronic structure calculation with a localized basis set. A few realistic examples are then considered.

## 2. General expression for the charge recombination reaction rate

For specificity, we consider the theory of CR rate in DSSCs, i.e. the process of neutralization of the oxidized dye by electron transfer from the conduction band of the semiconductor. This derivation follows that proposed in standard textbooks [32], but is required to provide the notation necessary to describe the charge transfer mediated by a molecular bridge, which is the new equation derived in this work. The initial state of this electron transfer process is an electronic state where an electron is present in the semiconductor’s conduction band manifold ($l$), and the dye is positively charged. The manifold ($\nu$) collects all vibrational states of the system. These vibrations are localized on the dye or the solvent and are not affected by the specific state $l$ occupied in the
The initial vibronic states can therefore be indicated as $\{|l, v\}$. We denote with $m$ the final electronic state where there is no excess electron in the semiconductor’s conduction band and a neutral dye is present. When the system is in state $m$, the equilibrium position of the vibration on the dye/solvent is changed, and this set of vibrational states after the CR is indicated with $\{|m, w\}$, with the final vibronic states indicated as $\{|m, w\}$. The energy of each vibronic state can be expressed as the sum of electronic and vibrational energy ($E_{l,v} = \varepsilon_l + E_v, E_{m,w} = \varepsilon_m + E_w$). A schematic of the energy diagram is shown in figure 1, where, for the sake of simplicity, we show only one normal vibrational mode.

The total Hamiltonian for the system is given by

$$H = H_0 + \tilde{V},$$

$$H_0 = \sum_l (\varepsilon_l + E_v)|l, v\rangle\langle l, v| + (\varepsilon_m + E_w)|m, w\rangle\langle m, w|$$

and

$$\tilde{V} = \sum_l \tilde{V}_{lm}|l, v\rangle\langle m, w| + \text{h.c.},$$

where $H_0$ represents the Hamiltonian where there is no interaction between initial and final states. The coupling $\tilde{V}$ stands for an electronic coupling between states $l$ and $m$, and the form used in equation (2.1c) implies that the Condon approximation has been used, i.e. $\langle l, v|\tilde{V}|m, w\rangle = \langle v|\tilde{V}|l\rangle$. The coupling $\tilde{V}$ may indicate a direct coupling between states $l$ and $m$ but also an effective coupling due to the coupling of states $l$ and $m$ to a bridge that connects them. The derivation in this section is indifferent to the origin of the coupling $\tilde{V}$, which is discussed instead in §3.

The total rate for the CR, i.e. for all transitions $|l, v\rangle \rightarrow |m, w\rangle$, is the sum over the possible initial and final states weighted by the occupation of the initial states,

$$k_{|l, v\rangle \rightarrow |m, w\rangle} = \sum_{l,v} P_{\mu,T}(\varepsilon_l) P_T(E_v) \sum_w k_{l,v \rightarrow m,w}.$$  

Here $P_{\mu,T}(\varepsilon_l)$ is the probability of occupation of a state in the semiconductor with energy $\varepsilon_l$, a function of the chemical potential $\mu$ in the semiconductor and the temperature $T$; and $P_T(E_v)$ is the probability that the vibrational level with energy $E_v$ is occupied. With the Hamiltonian defined above, we have

$$k_{l,v \rightarrow m,w} = \frac{2\pi}{\hbar} |\langle l, v|\tilde{V}|m, w\rangle|^2 \delta(E_{m,w} - E_{l,v})$$

$$= \frac{2\pi}{\hbar} |\langle v|\tilde{V}|l\rangle|^2 \delta(\varepsilon_m - \varepsilon_l + E_w - E_v).$$

\[\text{Figure 1. (a) Schematic of the electronic initial states } \{|l\}, \text{ forming a continuum band, and the final discrete state } m. \text{ (b) Representation of the vibronic levels for one of the initial electronic states } l \text{ and the final state } m.\]
and the total rate is
\[
k_{\{l,v\} \rightarrow \{m,w\}} = \frac{2\pi}{\hbar} \sum_l P_{\mu,T}(\epsilon_l) |\bar{V}_{lm}|^2 \sum_{v,w} P_T(E_v) |\langle v|w\rangle|^2 \delta(\epsilon_m - \epsilon_l + E_w - E_v)).
\] (2.4)

The second summation in equation (2.4) is known as the thermally and Franck–Condon averaged density of vibrational states:
\[
F(\epsilon_m - \epsilon_l) = \sum_{v,w} P_T(E_v) |\langle v|w\rangle|^2 \delta(\epsilon_m - \epsilon_l + E_w - E_v).
\] (2.5)

The expression for the total rate can then be rewritten as
\[
k_{\{l,v\} \rightarrow \{m,w\}} = \frac{2\pi}{\hbar} \sum_l P_{\mu,T}(\epsilon_l) |\bar{V}_{lm}|^2 F(\epsilon_m - \epsilon_l)
\]
\[
= \frac{2\pi}{\hbar} \sum_l \int dE f_\mu(E) |\bar{V}_{lm}|^2 F(\epsilon_m - E) \delta(E - \epsilon_l)
\]
\[
= \int dE f_\mu(E) \left[ \frac{2\pi}{\hbar} \sum_l |\bar{V}_{lm}|^2 \delta(E - \epsilon_l) \right] F(\epsilon_m - E)
\]
\[
= \int dE f_\mu(E) \bar{\Gamma}(E) F(\epsilon_m - E).
\] (2.6)

The probability of an electronic level being occupied is given by the product of the density of states at that energy with the Fermi–Dirac distribution \(f_\mu(E)\) (where the temperature dependence is understood). The spectral density \(\bar{\Gamma}(E)\) has been defined as
\[
\bar{\Gamma}(E) = \frac{2\pi}{\hbar} \sum_l |\bar{V}_{lm}|^2 \delta(E - \epsilon_l).
\] (2.7)

This quantity can be considered a measure of the facility of electron transfer between state \(l\) and state \(m\) at energy \(E\) and in the absence of nuclear modes. It would correspond exactly to the lifetime of a state prepared initially in \(m\) and degenerate with the levels \(\{l\}\). This latter situation was investigated in reference [33].

The Franck–Condon term \(F\) can be evaluated analytically if the vibrational wave functions are assumed to be displaced harmonic oscillators. In the limit of high temperature, when these oscillators can be treated classically, the Franck–Condon term takes a particularly simple form [34]:
\[
F(x) = \frac{1}{\sqrt{4\pi \lambda k_BT}} \exp \left[ -\frac{(x + \lambda)^2}{4\lambda k_BT} \right],
\] (2.8)

where \(\lambda\) represents the reorganization energy (a measure of the geometry change between states \(l\) and \(m\)) and \(k_BT\) is the thermal energy.

### 3. Bridge-mediated semiconductor–dye electronic coupling

In §2, we have considered the states \(\{l\}\) and \(m\) as directly coupled by an effective coupling \(\bar{V}\). Here, we consider more specifically the situation of semiconductor states coupled directly with the dye or through states localized on the bridge. The total electronic Hamiltonian can therefore be written as the sum of the electronic Hamiltonians on the semiconductor \((H^S_{el})\), the bridge \((H^B_{el})\) and the
molecule ($H_M^{el}$) plus the interactions between these three subsystems ($V = V_{SB}^{el} + V_{SM}^{el} + V_{BM}^{el}$), i.e.

$$H_{el}^{S} = \sum_{l \in L} \epsilon_l |l\rangle \langle l|, \quad H_{el}^{B} = \sum_{b \in B} \epsilon_b |b\rangle \langle b| + \sum_{b \neq b', b' \in B} V_{bb'} |b\rangle \langle b'|, \quad H_{el}^{M} = \epsilon_m |m\rangle \langle m|$$  \hspace{1cm} (3.1a)

$$H_{el}^{S} = \sum_{l \in L} \psi_{bl} |l\rangle \langle b|, \quad H_{el}^{B} = \sum_{b \in B} \gamma_{bl} |b\rangle \langle l|, \quad V_{el}^{SB} = \sum_{l,b \in L} \tau_{lb} |l\rangle \langle b| G |b'\rangle \langle b'| V_{el}^{BM} = \sum_{b \in B} \kappa_{bm} |b\rangle \langle m|.$$  \hspace{1cm} (3.1b)

and

A graphical representation of this system is given in figure 2.

A number of techniques (perturbation theory [35], scattering theory [29], partitioning methods [36], Green’s function methods [37–39]) have been used to express the effective coupling between subsystems $S$ and $M$ in an effective Hamiltonian that does not contain the bridge states explicitly, i.e.

$$H_{el}^{S} + H_{el}^{M} + \tilde{V}_{el}^{SM}. \quad \hspace{1cm} (3.2)$$

Here, we consider the effective coupling operator expressed from scattering theory as

$$\tilde{V} = V_{el} + V_{el}^{el} G V_{el}, \quad \hspace{1cm} (3.3)$$

where the retarded Green’s function operator can be defined as $G = (E + i \eta I - H_{el})^{-1}$ with $I$ being the identity operator, $E$ an independent variable and $\eta$ a real positive infinitesimal. The effective coupling between states $l$ and $m$ is

$$\langle l| \tilde{V} |m\rangle = \langle l| V_{el} |m\rangle + \sum_{b,b' \in B} \langle l| V_{el}^{SB} |b\rangle G |b'\rangle \langle b'| V_{el}^{BM} |m\rangle. \quad \hspace{1cm} (3.4a)$$

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**Figure 2.** (a) Schematic of the energy levels of the semiconductor, the bridge and the molecule and their coupling. (b) Physical partition of the systems into semiconductor, bridge and adsorbed molecule, which approximately corresponds to the partition of the Hamiltonian. (Online version in colour.)
The first term on the right-hand side of equation (3.4a) takes care of the direct coupling between the initial and final electronic states. The second term accounts for the bridge-mediated contribution to the electron transfer process, with the tunnelling probability across the bridge being given by the Green’s function matrix elements.

The Green’s function operator for a bridge interacting with the semiconductor slab and the molecular fragment attached to it can be recast in terms of the Green’s function for the non-interacting bridge plus a self-energy contribution that collects the perturbative effects on the bridge subsystem due to the interaction [40]; an expression for the self-energy has been reported elsewhere [41]. Because the introduction of the self-energy in the calculation of the bridge’s Green’s function would further complicate the theory without impacting on the results that will be presented (consistently with the weak semiconductor–bridge coupling regime), we approximate it as \( G_B(E) \approx G_B^0(E) \) where \( G_B \) is the matrix whose elements appear in equation (3.4a).

For the case of a non-orthogonal basis set, the Green’s function for the non-interacting bridge can be computed as \( G_B^0 = \left((E + i\eta)S_B^{-1} - S_B^{-1}H_B^0S_B^{-1}\right)^{-1} \) [42], where \( S_B \) is the overlap matrix over the bridge states. We can then compute the effective coupling by

\[
\tilde{V}_{lm} = \gamma_{lm} + \sum_{a,b,c,d} \tau_{ab} S_{ab}^{-1} G_B^0 S_{cd}^{-1} \kappa_{dm} \equiv \gamma_{lm} + \sum_{b,b'} \tau_{bb'} \delta_{bb'} \kappa_{b'm},
\]

where the indices run over the bridge states, and the Green’s function weighted by the overlap matrices has been indicated with the symbol \( \delta_{bb'} \) to lighten the notation. The next step is to compute the spectral density \( \tilde{\Gamma}(E) \) using the effective coupling expression above.

In the absence of a bridge (or if we assume all states of the bridge as part of the dye), we have \( \tilde{V}_{lm} = \gamma_{lm} \) and the spectral density \( \tilde{\Gamma}(E) \) can be expressed as [43]

\[
\tilde{\Gamma}(E) = \frac{2\pi}{\hbar} \sum_l |\gamma_{ml}|^2 \delta(E - \epsilon_l). \tag{3.5}
\]

In the presence of the bridge, the direct coupling is very small (because it decreases exponentially with distance) and so it is reasonable to neglect the direct coupling \( \gamma_{lm} \), i.e.

\[
\tilde{V}_{lm} = \sum_{b,b'} \tau_{bb'} \delta_{bb'} \kappa_{b'm}. \tag{3.6}
\]

The modulus squared of the coupling is given by

\[
\tilde{V}_{lm}^* \tilde{V}_{ml} = \sum_{b,b'} \tau_{bb'} \delta_{bb'} \kappa_{b'm} \sum_{a,a'} \kappa_{a'm}^{\dagger} \kappa_{a'm} \tau_{al} \tau_{al}^{\dagger} \tag{3.7}
\]

and the spectral density reads

\[
\tilde{\Gamma}(E) = \frac{2\pi}{\hbar} \sum_l \sum_{b,b'} \tau_{bb'} \delta_{bb'} \kappa_{b'm} \sum_{a,a'} \kappa_{a'm}^{\dagger} \kappa_{a'm} \tau_{al} \tau_{al}^{\dagger} \delta(E - \epsilon_l) \tag{3.8}
\]

where, for the last equality, we have introduced the semiconductor’s spectral density

\[
\Gamma_{ab}(E) = \frac{2\pi}{\hbar} \sum_l \tau_{al}^{\dagger} \tau_{al} \delta(E - \epsilon_l). \tag{3.9}
\]

By further defining \( K_{a'b'}^{\dagger} = \kappa_{b'm}^{\dagger} \kappa_{a'm} \), we obtain

\[
\tilde{\Gamma}(E) = \sum_{a,a'} \sum_{b,b'} \Gamma_{ab} \delta_{bb'} \kappa_{a'm}^{\dagger} \kappa_{a'm} \tau_{al} \tau_{al}^{\dagger} = \text{tr} [\Gamma g K g^{\dagger}], \tag{3.10}
\]

where \( \text{tr}[\cdot] \) denotes the trace operator over the bridge states and the bold type has been used for the matrices involved (whose size is the total number of bridge states present).

Equation (3.10) is one of the main results of this work. This is the form of the spectral density that should be used in the expression for the rate equation (2.6) when the coupling between

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\]

\[
\tilde{V}_{lm} = \sum_{b,b'} \tau_{bb'} \delta_{bb'} \kappa_{b'm}. \tag{3.6}
\]

\[
\tilde{V}_{lm}^* \tilde{V}_{ml} = \sum_{b,b'} \tau_{bb'} \delta_{bb'} \kappa_{b'm} \sum_{a,a'} \kappa_{a'm}^{\dagger} \kappa_{a'm} \tau_{al} \tau_{al}^{\dagger} \tag{3.7}
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\]

\[
\Gamma_{ab}(E) = \frac{2\pi}{\hbar} \sum_l \tau_{al}^{\dagger} \tau_{al} \delta(E - \epsilon_l). \tag{3.9}
\]

\[
\tilde{\Gamma}(E) = \sum_{a,a'} \sum_{b,b'} \Gamma_{ab} \delta_{bb'} \kappa_{a'm}^{\dagger} \kappa_{a'm} \tau_{al} \tau_{al}^{\dagger} = \text{tr} [\Gamma g K g^{\dagger}], \tag{3.10}
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\]

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\tilde{V}_{lm}^* \tilde{V}_{ml} = \sum_{b,b'} \tau_{bb'} \delta_{bb'} \kappa_{b'm} \sum_{a,a'} \kappa_{a'm}^{\dagger} \kappa_{a'm} \tau_{al} \tau_{al}^{\dagger} \tag{3.7}
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\Gamma_{ab}(E) = \frac{2\pi}{\hbar} \sum_l \tau_{al}^{\dagger} \tau_{al} \delta(E - \epsilon_l). \tag{3.9}
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\]
semiconductor and dye is mediated by a bridge. The spectral density $\tilde{\Gamma}(E)$ includes a matrix $\Gamma$ (that quantifies the coupling between semiconductor and bridge), a matrix $K$ (that quantifies the coupling between bridge and dye) and the Green’s function matrix $g$ (that expresses the propagation across the bridge). As we mentioned in §2, $\tilde{\Gamma}(E)$ would also be the rate of CI (tunnelling) of a state initially prepared in $m$ and degenerate with the manifold $\{l\}$. It is therefore particularly appealing that the form obtained for $\tilde{\Gamma}(E)$ is very similar to the standard Landauer formula for the transmittance across a molecular system connected to two electrodes [44]. In the Landauer formula, instead of the matrix $K$, there is another term such as $\Gamma$, describing the coupling with a second electrode.

The aim of this paper is to produce a formalism that can be applied in conjunction with electronic structure computations of the system of interest. The semiconductor–molecule interface can be routinely simulated, and, for typical chemical applications, the Hamiltonian and overlap matrices are expressed in terms of a localized, non-orthogonal basis set, such as a linear combination of atomic orbitals. Therefore, if we consider the chromophore unit, we can identify the state $|m\rangle$ with the isolated molecule’s highest occupied molecular orbital (HOMO), which can be expanded in terms of the localized basis set as: $|m\rangle = \sum c_j^m |\phi_j\rangle$. The coupling between bridge states and state $|m\rangle$ can be expressed in terms of these localized states:

$$\kappa_{bm} = \langle b | V_{BM}^{el} | m \rangle = \sum_j c_j^m \langle b | V_{BM}^{el} | \phi_j \rangle. \quad (3.11)$$

The bridge not only mediates the coupling between chromophore and semiconductor, but also produces effects of quantum interference. If more than one orbital localized on the bridge is coupled to the electrode, then different tunnelling pathways are possible and they may interfere constructively or destructively [45]. Destructive interference gives rise to very low dips in the function $\tilde{\Gamma}(E)$ at special energies that are known as antiresonances. Energies where $\tilde{\Gamma}(E)$ is maximum are known as resonances and occur when the energy is degenerate with one of the bridge orbital levels [46].

4. Charge recombination rate calculations for realistic dyes

To exemplify the methodology, we compute for example the CR rate for the series of dyes reported in figure 3 with bridges of different length. In these dyes, the coupling between bridge and chromophore is particularly weak, as described in detail in [20], and the partitioning method proposed above should be particularly suitable. The length of the bridge will allow us to disregard the direct coupling contribution.

The electronic structure calculation for the evaluation of the spectral density in equation (3.10) proceeds in two steps: using the SIESTA code [47], we have simulated independently (i) the isolated TiO$_2$ slab, and (ii) the whole system semiconductor plus dye. The anatase (101) surface was modelled using a $3 \times 3$ surface supercell containing 108 atoms and four atomic layers. Geometry relaxation was performed while keeping the coordinates of the bottom atomic layer fixed at the values of the bulk phase. The Brillouin zone was then sampled in 48 $k$-points (this density of the $k$-point grid was obtained by setting the cut-off parameter in SIESTA to 30 Å). The electronic structure was computed with a GGA–PBE exchange and correlation functional with double-zeta basis set and Troullier–Martins pseudo-potential. A similar geometry optimization was also carried out in the presence of formic acid in order to establish the adsorption geometry of the dye’s anchoring group. The rest of the dye molecule was attached to the carboxylic group preserving the relative orientation. Single point energy calculations were then performed at the same level of theory but including only the $\Gamma$-point on the slab plus adsorbate system shown in figure 2 in order to obtain the matrix elements of the full Hamiltonian operator equation (3.1a). This last calculation was performed at the $\Gamma$-point only, because we are not considering a periodic array of dyes interacting with each other, but rather only one dye adsorbed on a periodic semiconductor surface.
Figure 3. Chemical structure of the dyes considered.

Figure 4. Spectral density for the dyes considered. The energy range that contributes most to the rate is highlighted assuming a sharp limit for the conduction band at $-4.06$ eV (shaded). (Online version in colour.)

The semiconductor’s Hamiltonian matrix $H_{el}^{sl}$ was obtained from the isolated slab calculation and it has been used to evaluate the semiconductor’s eigenvalues required in equation (3.9). The simulation of the semiconductor plus dye system allowed us to extract from the total Hamiltonian matrix the semiconductor–bridge and the bridge–chromophore coupling matrix elements (indicated with $\tau$ and $\kappa$, respectively, in §3), together with the bridge’s Hamiltonian matrix $H_{el}^{bl}$. The use of a localized basis set makes it possible to partition the dye molecule (and its Hamiltonian) into the bridge and chromophore fragments as required by our theoretical scheme. The chromophore fragment has been identified as the aromatic core in figure 3, including the diphenylamino substituent; the bridge has been defined as the polyene chain, including the carboxylic anchor and the cyano group attached to it. The coefficients of the molecular orbital on the chromophore fragment, indicated by $c_{m}^{i}$ in equation (3.11), have been extracted from a similar single point energy calculation on the isolated dye.

In figure 4, we report the spectral densities for the sensitizers considered; $\tilde{\Gamma}(E)$ is shown as a function of the independent energy variable introduced in the definition of the Green’s operator. To improve the agreement between the position of the conduction band edge of the simulated system (in this case, the isolated slab) with the values attained experimentally in a DSSC (reported in [48]) we have acted on the semiconductor’s states with a scissors operator, leading to a shift of 0.6 eV in the conduction band states. We resort to this strategy because it is well known how problematic it can be to predict the correct energy alignment in these systems [49]. Furthermore, the conduction band edge position in DSSCs is susceptible to the presence of additives [50] or electrolytes [51] co-adsorbed on the semiconductor surface. By aligning the conduction band minimum with its experimental counterpart, we implicitly account for these experimental variables in our model [52]. The energy range relevant for the integral in equation (2.6) is highlighted in figure 4 by a shaded marker. A shift of this integration interval of 0.1 eV relative to the chosen energy scale does not change our conclusions. The spectral...
The density is a complicated function of the bridge’s electronic Hamiltonian (which also reflects the chemical connectivity between its atoms) and the coupling matrices with the other subsystems. The occurrence of peaks, as mentioned before, is related to the bridge’s eigenvalues, whereas the antiresonances are associated with signatures of quantum interference. If a model system is studied, with the interaction restrained to the bridge’s terminal sites, then antiresonances do not appear, whereas, if the electron is allowed to hop on different bridge orbitals and then to propagate across, then the molecule interference is generated [45].

The position of the peaks in figure 4 relates well with the bridge’s eigenenergies: by changing the length of the bridge, we are effectively modifying the energy spectrum of that subsystem, hence shifting the energies at which the peaks are located. The presence of antiresonances is associated with the anchoring group used and with its coupling to the semiconductor. Interestingly, a sharp interference feature appears close to the conduction band edge, and it is not affected by changing the length of the bridge. The presence of this antiresonance is associated with the anchoring group used and with its coupling to the semiconductor. In particular, this feature is associated with the different symmetry of the states occurring in that energy range and it disappears when the calculation is done on a hypothetical model molecule without an anchoring group and coupled only through the terminal atom to the electrode. This is possibly an explanation for the success of the carboxylic acid anchoring group in DSSCs, because having an antiresonance located in this energy range is going to slow down the CR to the oxidized dye.

Experimental investigations are particularly suited to obtain the lifetimes of the processes taking place in DSSCs. We report our results in terms of the recombination lifetime, $\tau_{\text{CR}}$, defined as the reciprocal of the reaction rate in equation (2.6). Besides the spectral density, other quantities are required to calculate $\tau_{\text{CR}}$: these are the chemical potential $\mu$ in the semiconductor, the reorganization energy $\lambda$ associated with the nuclear and dielectric rearrangements involved with the charge transfer and the free-energy variation $\varepsilon_m$ of the molecular moiety. The value of the chemical potential is chosen to be 0.2 eV below the conduction band edge to mimic an out-of-equilibrium electron population within the conduction band states. This value lies within the experimental range attained for typical DSSC architectures [53]. The quantities $\varepsilon_m$ and $\lambda$ have been evaluated following the computational procedure in [52] for the molecules in figure 3; their values vary only marginally along the series (by 0.1 and 0.05 eV, respectively). This suggests that, to simplify the analysis of the results and to focus on the impact of the spectral density on the rate, we can fix these two quantities to the values $\lambda = 0.4$ eV and $\varepsilon_m = -5.0$ eV, i.e. the average for the molecules considered.

The values obtained for the CR lifetime $\tau_{\text{CR}}$ are reported in figure 5. The data show an exponential increase with the length of the bridge fragment, which is defined as the distance...
between the carbon atom of the anchoring group and that in the pyrene core linked to the bridge. If the data are fitted to the exponential \( \tau_{CR} = \tau_0 \exp(-\beta R) \), where \( R \) is the bridge length, then we obtain \( \beta = 0.1 \text{ Å}^{-1} \) in complete agreement with the value reported for similar systems [54]. This dependence on the distance is not unexpected: it was first derived by Beratan for tight binding model Hamiltonians [55], and it has been related to the imaginary part of the band structure in Green's function-oriented studies of metal–organic chain interfaces [56]. The underpinning assumption in the latter approach is that the molecular environment in the bridge portion can be approximated by that of an infinite chain, disregarding the modifications due to the interaction with the interface. This type of approximation is not required in the present scheme, as we explicitly account for the bridge portion, which does not have to be made up by periodically repeated units. The impact on the CR lifetime is rather weak: increasing the bridge length by 10 Å has slowed down the CR only by a factor 3 for the range of molecules considered. Therefore, increasing the length of the bridge fragment is going to have a modest impact on the performances of the DSSCs, as confirmed by experiment [57]. Moreover, by increasing the length of the bridge, the coupling between the semiconductor and the lowest unoccupied molecular orbital (LUMO) of the neutral molecule, responsible for the CI process, is most likely to get smaller, hence reducing the quantum efficiency for the CI. A strategy to slow down the CR without affecting the injection process has been developed recently [20] without imposing any constraints on the bridge’s chemical structure: only the attachment to the chromophore unit plays a role. On the other hand, the theory presented in this study will enable modifications to the chemical connectivity in the bridge unit to be considered explicitly.

The electron transfer processes taking place in DSSCs depend critically on the characteristics of the semiconductor surface: for instance, the presence of trap states is known to speed up the CR reaction by creating a localized state below the conduction band edge that has faster recombination kinetics in the Marcus inverted region [58]. This extra electronic state may well affect the term in equation (3.10) responsible for the coupling between the semiconductor and the bridge’s anchor. However, it is reasonable to assume that, for a fixed defect position, this term will be equally modified for all the bridges considered here, hence the CR rate will show the same dependence on the bridge length.

5. Conclusion

In this paper, we have derived an expression for the rates of the CR process taking place at the semiconductor–molecule interface in a DSSC. In particular, we have developed a formalism that allows the study of CR mediated by a molecular bridge that connects the chromophore with the semiconductor. The main result is a combination of Marcus theory of electron transfer at the interface and the theory of electron transport in molecular junctions, with several interesting similarities found between the Landauer formula and the expression of the rate. From the practical point of view, this formalism can be used to explore the effect of changing the bridge on the rate of interfacial electron transfer. The formalism was designed to be coupled with density functional theory (DFT) electronic structure calculation and was exemplified with the calculation of the CR rate for a series of systems that differ in the length of the bridge. The choice of this particular level of theory, regarded as a good compromise in terms of computational constraints, is subjected to well-known shortcomings, stemming from limitations in the DFT implementation used [59] and the basis set used [60], which have been amply addressed in the literature on molecular electronics. Besides computational limitations, other uncertainties, when comparing the results presented with experimental realizations, might stem from the breakdown of the Condon approximation [61], thermal fluctuations of the energy levels [62], inaccuracies in the computational scheme for the reorganization energy [63], and geometrical distortions [64] from the ideal case analysed here. As mentioned beforehand, modifications in the electrolyte composition may also impact on the energy alignment across the interface: for the dye families considered experimentally and to benchmark our model, however, the range of values typically attained is generally quite modest [52].
In future studies, the same formalism can be used to explore the possible role of interference in the process of interfacial electron transfer in any system (not necessarily DSSCs) containing a chromophore connected to a semiconductor via a molecular bridge.

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References


