Transport and optical response of molecular junctions driven by surface plasmon-polaritons

Maxim Sukharev\textsuperscript{1,} and Michael Galperin\textsuperscript{2,}\textsuperscript{*}

\textsuperscript{1}Department of Applied Sciences and Mathematics, Arizona State University at the Polytechnic Campus, Mesa, AZ 85212, USA
\textsuperscript{2}Department of Chemistry \& Biochemistry, University of California at San Diego, La Jolla, CA 92093, USA

(Dated: November 12, 2009)

We consider a biased molecular junction subjected to external time-dependent electromagnetic field. The field for two typical junction geometries (bowtie antennas and metal nanospheres) is calculated within finite-difference time-domain technique. Time-dependent transport and optical response of the junctions is calculated within non-equilibrium Green’s function approach expressed in a form convenient for description of multi-level systems. We present numerical results for a two-level (HOMO-LUMO) model, and discuss influence of localized surface plasmon polariton modes on transport.

PACS numbers: 85.65.+h 73.63.Kv 78.67.Hc 78.20.Bh

I. INTRODUCTION

Optical properties of structures composed of noble metals have long been attracting a considerable attention due to unique features of such systems in the visible spectrum.\textsuperscript{1-4} Recent advances in fabrication techniques along with a tremendous progress in laser technologies opened new venues for application of plasmonic materials in biology,\textsuperscript{5} integrated optics,\textsuperscript{6} nanoscale imaging,\textsuperscript{7} and single molecule manipulation.\textsuperscript{8} Physics of surface plasmon phenomenon is relatively simple and has long been studied.\textsuperscript{9,10} In brief, coherent oscillations of conductive electrons in a skin-layer of metal known as plasmons are capable of producing strong local electromagnetic (EM) fields in the near-field region. It has been reported that such ”hot” spots can be localized within 10 nm or less. This along with a great sensitivity to initial conditions and geometry makes plasmonic structures so attractable for atom/molecule manipulations.

A natural combination of nanoplasmonics and molecular response to the generated field started to appear as molecular nanopolaritons,\textsuperscript{11,12} which studies molecular influence on field propagation, and as a tool for developing molecular switches.\textsuperscript{13} The latter utilizes nonadiabatic alignment of a molecule on semiconductor surface under a tip of scanning tunneling microscope.

Recent developments in experimental techniques capable of measuring optical response of current-carrying molecular junctions\textsuperscript{14,15} lead to theoretical formulations suitable for simultaneous description of both transport and optical properties of molecular devices.\textsuperscript{16,17}

While experimental data are measured in real time, theoretical description of both transport and optical response so far has mostly been focused on a steady-state description. Time-dependent transport usually is treated either within kinetic theory\textsuperscript{18,19} or within time-dependent density functional approach.\textsuperscript{20-22} The former generally misses broadening of molecular states due to coupling to macroscopic contacts,\textsuperscript{23,24} and information on coherence\textsuperscript{25} although interesting generalizations started to appear.\textsuperscript{26} Limitations of the latter are due to absence of developed pseudopotentials and fundamental necessity to treat finite (closed) systems (see e.g. Ref. 30 for discussion). An alternative approach, based on non-equilibrium Green function (NEGF) technique, was initially formulated in Refs. 31,32,33. This approach is a natural choice for description of open non-equilibrium systems. Moreover it provides possibility to describe response of a molecular junction initially under bias to external time-dependent perturbation (e.g. laser field).

Here we consider influence of external field specific for particular geometry on transport properties and optical response of molecular junction. While formulation of time-dependent transport within NEGF is general\textsuperscript{34,35} all the applications so far were restricted to resonant single level models only. We propose a variant of the scheme capable of dealing with many-level systems. The exact calculations are compared to adiabatic pumping regime, frequent in the literature on time-dependent transport\textsuperscript{36,37} were at the lowest order the problem is reduced to a set of quasi-steady-state solutions with time dependent (slow timescale) parameters. Also we generalize our previous consideration of steady-state optical response of current-carrying junctions\textsuperscript{38,39} to a time-dependent situation.

The paper is organized as follows. Section II presents a model of molecular junction. Section III describes methodology of EM field calculation. Section IV describes methodology for simulating transport through molecular junction subjected to external time-dependent field. Adiabatic pumping version is discussed in section V. Numerical results are presented in section VI. Section VII concludes.

II. MODEL

We consider a two-level system $\varepsilon_{1,2}$, representing highest occupied (HOMO) and lowest unoccupied (LUMO)
molecular orbitals (or ground and excited states in the many-body language), coupled to two macroscopic electrodes \( L \) and \( R \). The electrodes are considered to be each in its own equilibrium with electrochemical potentials \( \mu_L \) and \( \mu_R \), respectively. We assume that the driving (laser field) frequency is smaller than the plasma frequency, so that usual division of the junction into nonequilibrium molecule coupled to free electron reservoirs (metallic contacts) is relevant (for a thorough discussion of the assumptions see Ref. [31]). Local field at the position of the molecule is calculated within finite difference time domain technique (see section [IV] for details), and is assumed to be an external time-dependent driving force causing (de)excitation in the molecule. Following Ref. [37] in addition to charge transfer between contacts and molecule we introduce also energy transfer (coupling of molecular excitations to electron-hole excitations in the contacts). Molecular excitations are coupled to a bath of free photon modes (accepting modes), which serve as a measurement device of molecular optical response. Hamiltonian of the system is

\[
\hat{H} = \hat{H}_0 + \hat{V} = \sum_{i=1,2} \varepsilon_i \hat{d}_i^\dagger \hat{d}_i - \left( \mu_{12} \hat{d}_1^\dagger \hat{d}_2 + \mu_{21} \hat{d}_2^\dagger \hat{d}_1 \right) \hat{E}(t) + \sum_{k \in \{L,R\}} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k + \sum_{\alpha} \omega_{\alpha} \hat{a}_\alpha^\dagger \hat{a}_\alpha + \sum_{i=1,2, k \in \{L,R\}} \left( V_{ki}^{\text{et}} \hat{c}_k^\dagger \hat{d}_i + V_{ki}^{\text{et}} \hat{d}_i^\dagger \hat{c}_k \right) \tag{2}
\]

\[
\hat{V} = \sum_{k \neq k' \in \{L,R\}} \left( \hat{V}_{kk'}^{\text{eh}} \hat{c}_k^\dagger \hat{c}_{k'} \hat{d}_1^\dagger \hat{d}_2 + \hat{V}_{kk'}^{\text{eh}} \hat{c}_{k'}^\dagger \hat{c}_k \hat{d}_1 \hat{d}_2^\dagger \right) + \sum_{\alpha} \left( \hat{V}_\alpha \hat{a}_\alpha^\dagger \hat{d}_1^\dagger \hat{d}_2 + \hat{V}_\alpha^* \hat{a}_\alpha \hat{d}_1^\dagger \hat{d}_2^\dagger \right) \tag{3}
\]

Here \( \hat{d}_i^\dagger \) (\( \hat{d}_i \)) and \( \hat{c}_k^\dagger \) (\( \hat{c}_k \)) are creation (annihilation) operators for an electron in the state \( i \) of the molecule and state \( k \) of the contact, respectively. \( \hat{d}_i^\dagger \) \( \hat{a}_\alpha \) is creation (annihilation) operator for a photon in the state \( \alpha \). \( \hat{E}(t) \) is external time-dependent field, and \( \mu_{ij} = \langle i | \hat{p} | j \rangle \) is matrix element of the molecular (vector) dipole operator between states \( i \) and \( j \) of the molecule (\( i,j = 1,2 \)). We assume \( \mu_{11} = \mu_{22} = 0 \) (or alternatively one can think about these contributions being included into definition of the state energies \( \varepsilon_{1,2} \)). \( V_{\text{et}} \) and \( V_{\text{en}} \) are matrix elements for electron and energy transfer between molecule and contacts, and \( V_p \) represents optical response of the molecule.

Below we discuss two approaches to transport and optical response simulations within the model: exact solution of the time-dependent Dyson equation and adiabatic pumping regime. The former is similar to the procedure described in Refs. [31,62,53] however it is presented in a form convenient for treating a multi-level molecular system (see section [V] for discussion). The latter assumes that \( \hat{E}(t) \) can be represented as a product of an oscillation of frequency \( \omega_0 \) with a slowly varying in time (on the timescale of \( \omega_0 \)) envelope \( \hat{F}(t) \). In the spirit of the Born-Oppenheimer approximation \( F(t) \) is considered as a parameter when solving electronic part of the problem. In this case the form of molecule-field interaction becomes (within rotating wave approximation)

\[
- \left( \mu_{12} \hat{d}_2 e^{i\omega_0 t} + \mu_{21} \hat{d}_1 e^{-i\omega_0 t} \right) \hat{F}(t) \tag{4}
\]

Details of the approach are presented in section [V].

As usual, we treat the perturbation \( \hat{V} \), Eq. (3), at the second order and within noncrossing approximation.

Self-energy due to energy transfer (on the Keldysh contour) is given by

\[
\Sigma_{ep}(\tau_1, \tau_2) = \sum_{k \neq k' \in \{L,R\}} \left| V_{kk'} \right|^2 g_k(\tau_2, \tau_1) g_{k'}(\tau_1, \tau_2) \left[ \begin{array}{cc} G_{22}(\tau_1, \tau_2) & G_{21}(\tau_1, \tau_2) \\ G_{12}(\tau_1, \tau_2) & G_{11}(\tau_1, \tau_2) \end{array} \right] \tag{5}
\]

where \( G_{ij} \) are molecular Green functions in the lowest order of expansion associated with the Hamiltonian \( \hat{H}_0 \), Eq. (2), and \( g_k \) are Green functions of free electrons in the contacts. Self-energy due to coupling to photon bath is given by

\[
\Sigma_{p}(\tau_1, \tau_2) = \sum_{\alpha} \left| V_{\alpha} \right|^2 \left[ \begin{array}{c} \int_{\tau_1}^{\infty} dt' F_{\alpha}(t_1 - t') \rho_{21}(t') \delta(\tau_1, \tau_2) \\ \int_{-\infty}^{\tau_1} dt' F_{\alpha}^*(t_1 - t') \rho_{12}(t') \delta(\tau_1, \tau_2) \end{array} \right] \tag{6}
\]

III. ELECTROMAGNETIC FIELD SIMULATIONS

Among various numerical techniques that allow one to predict optical properties of plasmonic systems the finite-difference time-domain approach (FDTD) is con-
sidered to be the most efficient and yet relatively simple. FDTD yields data in perfect agreement with experimental measurements and results obtained within other techniques. We simulate optical response of metal structures utilizing FDTD approach, in which Maxwell equations are discretized in space and time following Yee’s algorithm. Dispersion of dielectric constant of metal, $\varepsilon(\omega)$, is taken in the form of the Drude model
\begin{equation}
\varepsilon(\omega) = \varepsilon_r - \frac{\omega_p^2}{\omega^2 - i\Gamma \omega}
\end{equation}
with numerical parameters describing silver for the wavelengths of interest $\varepsilon_r = 8.26$, $\omega_p = 1.76 \times 10^{16}$ rad/sec, $\Gamma = 3.08 \times 10^{14}$ rad/sec.

For simulations of open systems, one needs to impose artificial absorbing boundaries in order to avoid reflection of outgoing EM waves back to the simulation domain. Among various approaches that address this numerical issue, the perfectly matched layers (PML) technique is considered to be the most adequate. It reduces the reflection coefficient of outgoing waves at the simulation region boundary to $10^{-8}$. Essentially, the PML approach surrounds the simulation domain by thin layers of nonphysical material that efficiently absorbs outgoing waves incident at any angle. We implement the most efficient and least memory intensive method, convolution perfectly matched layers (CPML) absorbing boundaries, at all six sides of the 3D modeling space. Through extensive numerical experimentation, we have empirically determined optimal parameters for the CPML boundaries that lead to almost no reflection of the outgoing EM waves at all incident angles. Spatial steps, $\delta x = \delta y = \delta z$, along all axes are fixed at 1 nm to assure numerical convergence and the temporal step is $\delta t = \delta x/(2c)$, where $c$ is the speed of light in vacuum.

Numerical integration of Maxwell equations on a grid within the FDTD framework was performed at the local ASU home-built supercomputer utilizing 120 processors. An average execution time for our codes is around 20 minutes.

A particular advantage of the FDTD method is its ability to obtain the optical response of the structure (assuming linear response) in the desired spectral range in a single run. The system is excited with an ultra-short optical pulse constructed from Fourier components spanning the frequency range of interest. Next, Maxwell’s equations are propagated in time for several hundred femtoseconds and the components of the EM field are detected at the point of interest (for our purposes we consider the detection point where a molecule is located). Fourier transforming the detected EM field on the fly yields intensities that can be easily processed into the spectral response. Since we also have access to the field components, we can evaluate the intensity enhancement relative to the incident field. This provides the capability for straightforward evaluation of ‘coupling efficiency’ of our plasmonic structures in the spectral range of interest.

IV. TIME-DEPENDENT TRANSPORT

We are interested in calculating time-dependent current and optical response of the junction. Expression for the current at the interface $K (K = L, R)$ between molecule and contact is
\begin{equation}
I_K(t) = \frac{e}{\hbar} \int_{-\infty}^{t} dt_1 \text{Tr} \left[ \Sigma_K^<(t_1, t_1) G^>(t_1, t_1) + G^<(t_1, t_1) \Sigma_K^>(t_1, t_1) \right]
\end{equation}
where $\Sigma_K$ is self-energy due to coupling to contact $K$
\begin{equation}
[\Sigma_K^{rt}(\tau_1, \tau_2)]_{ij} = \sum_{k \in K} V_{ik} g_{kj}(\tau_1, \tau_2) V_{kj}
\end{equation}
and $r, a, <, >$ are retarded, advanced, lesser, and greater projections respectively. In the wide band limit, when escape rate matrix
\begin{equation}
[\Gamma_K(E)]_{ij} = 2\pi \sum_{k \in K} V_{ik} V_{kj} \delta(E - \varepsilon_k)
\end{equation}
is assumed to be energy independent and real part of the self-energy is disregarded, and when time modulation is restricted to molecular subspace only, expression can be reduced to
\begin{equation}
I_K(t) = I_K^{in}(t) - I_K^{out}(t)
\end{equation}
\begin{equation}
I_K^{in}(t) = -\frac{e}{\hbar} \int_{-\infty}^{t} dE f_K(E) \text{ImTr} \left[ \Gamma_K A^r(t, E) \right]
\end{equation}
\begin{equation}
I_K^{out}(t) = +\frac{e}{\hbar} \text{ReTr} \left[ \Gamma_K \rho(t) \right]
\end{equation}
where $f_K(E)$ is Fermi-Dirac distribution in contact $K$ and $A^r(t, E)$ is time-dependent (one-sided) Fourier transform of the retarded Green function $G^r(t, t')$.

\begin{equation}
A^r(t, E) = \int_{-\infty}^{t} dt' e^{iE(t-t')} G^r(t, t')
\end{equation}
In the absence of time-dependent driving $A^r(t, E)$ reduces to usual Fourier transform for retarded Green function $G_0^r(E) = [E - H_0 - \Sigma^r(E)]^{-1}$. In general $\Sigma^r$ has contributions (additive within noncrossing approximation) from all the processes involved. $\rho(t)$ in (13) is reduced density matrix
\begin{equation}
\rho(t) = -i G^<(t, t)
\end{equation}
Lesser and greater Green functions are calculated from the time dependent Dyson equation
\begin{equation}
G^<;^>(t_1, t_2) = \int_{-\infty}^{t_1} dt_1 \int_{-\infty}^{t_2} dt_2 e^{-iE(t_1-t_2)} \times A^r(t_1, E) \Sigma^<;^>(E) A^a(t_2, E)
\end{equation}
where
\[ A_{ij}^\alpha(t, E) = A_{ji}^\alpha(t, E) \quad (17) \]
and \( A^\alpha(t, E) \) is defined in Eq. (14).

Contrary to our previous consideration\textsuperscript{36,37} optical response of molecular junction is calculated as a true photon flux into modes \( \{\alpha\} \), rather than corresponding electronic current between molecular orbitals. We start from general expression for time-dependent photon flux into mode \( \alpha \) (the derivation follows the corresponding procedure for electronic current, the latter can be found in e.g. Ref. 41)
\[
J^\alpha(t) \equiv \frac{d}{dt} < \hat{a}^\dagger_\alpha(t) \hat{a}_\alpha(t) > = |V^\alpha_p|^2 \int_{-\infty}^{t} dt_1 
\times \left[ G^\leq_\alpha(t_1, t_1) + G^>_\alpha(t_1, t_1) F^\leq_\alpha(t_1, t_1) - F^>_\alpha(t_1, t_1) G^\leq_\alpha(t_1, t_1) - G^\leq_\alpha(t_1, t_1) F^>_\alpha(t_1, t_1) \right] \quad (18)
\]

Here \( G \) is two-particle Green function
\[
G(\tau, \tau') \equiv -\frac{i}{\hbar} < \hat{D}(\tau) \hat{A}^\dagger(\tau') > \quad (19)
\]
where \( \hat{D} \equiv \hat{d}_1^\dagger \hat{d}_2 \) is molecular de-excitation operator. For empty accepting mode \( \alpha \) expression (13) reduces to
\[
J^\alpha(t) = -\frac{2 |V^\alpha_p|^2}{\hbar} \text{Im} \int_{-\infty}^{t} dt_1 e^{i\omega_\alpha(t_1-t)} G^\leq_\alpha(t_1, t_1) \quad (20)
\]
As in Ref. 37 we approximate the two-particle Green function by zero-order (in interaction) expression
\[
G^\leq_\alpha(t_1, t_1) \approx -i\hbar \left[ G^\leq_{11}(t_1, t_1) G^\leq_{22}(t_1, t_1) - \rho_{12}(t) \rho_{21}(t_1) \right] \quad (21)
\]
Note that if envelope change in time is slow (on the timescale of \( \omega_\alpha \)) second term on the right of (21) can be safely disregarded. In this case expression (20) becomes equivalent to approximate expression used in Ref. 37.

Below we calculate frequency resolved
\[
J(\omega, t) \equiv \sum_\alpha J^\alpha(t) \delta(\omega - \omega_\alpha) \quad (22)
\]
\[
\approx \frac{1}{\pi \hbar} \gamma_\alpha(\omega) \text{Re} \int_{-\infty}^{t} dt_1 e^{i\omega(t_1-t)} G^\geq_{11}(t_1, t_1) G^\leq_{22}(t_1, t_1)
\]
and total
\[
J_{\text{tot}}(t) \equiv \int_{0}^{\infty} d\omega J(\omega, t) \quad (23)
\]
photon fluxes. Here \( \gamma_\alpha(\omega) \equiv 2\pi \sum_\alpha \delta(\omega - \omega_\alpha) \), and in simulations we use
\[
\gamma_\alpha(\omega) = \eta \omega e^{-\omega/\omega_c} \quad (24)
\]
To calculate time-dependent charge, Eq. (11), and photon, Eq. (20), fluxes one needs time-dependent Fourier transform of retarded Green function, Eq. (13). The Dyson equation for retarded Green function is
\[
\left( \frac{\partial}{\partial t} - H(t) \right) G^r(t, t') = \left( \frac{\partial}{\partial t} - H(t) \right) G^a(t, t') \quad (25)
\]
Its one-sided Fourier transform leads to equation for \( A^r(t, E) \) in the form
\[
\left( \frac{\partial}{\partial t} - [H_0(t) - E] \right) A^r(t, E) = \int_{-\infty}^{+\infty} dt_1 \Sigma^r(t-t_1) A^r(t_1, E) = \mathbb{I} \quad (26)
\]
We consider situation when time-dependent external field is applied at time \( t_0 \) to a biased molecular junction initially at steady-state. In this case differential equation (26) can be solved numerically starting from known initial condition \( A^r(t_0, E) = G^r_0(\omega|E) = [E - H^0_0 - \Sigma^r(\omega)]^{-1} \).

Alternatively, splitting \( H_0(t) \) into time-independent \( H^0_0 \) and time-dependent \( H^0(t) \) parts (average over time of the time-dependent part can be included into the time-independent Hamiltonian), one can rewrite Dyson equation (26) in the integral form
\[
G^r(t, t') = G^r_0(t-t') + \int_{-\infty}^{+\infty} dt_1 G^r_0(t-t_1) H^0_0(t_1) G^r(t_1, t') \quad (27)
\]
One-sided Fourier transform of (27) leads to integral equation for \( A^r(t, E) \)
\[
A^r(t, E) = G^r_0(E) \quad (28)
\]
\[
+ \int_{t_0}^{t} dt_1 G^r_0(t-t_1) e^{i\omega(t-t_1)} H^0(t_1) A^r(t_1, E) \quad (29)
\]
where lower limit of the integral in the right is set to \( t_0 \) since \( H^0(t) \) for \( t < t_0 = 0 \). Its solution is
\[
A^r(t, E) = U_{\text{eff}}(t, t_0; E) G^r_0(E) \quad (30)
\]
Effective evolution operator \( U_{\text{eff}} \) can be obtained by variety of methods available in the literature (see e.g. Ref. 10 and references therein). One of the simplest schemes is cumulant (or Magnus) expansion\textsuperscript{22,29,40}.

Note that although our consideration is restricted to the case when time-dependent driving takes place in the molecular subspace only, generalization to driving in the contacts or at the molecule-contact interface is straightforward.

V. ADIABATIC PUMPING REGIME

When time evolution of an envelope \( \tilde{F}(t) \), Eq. (4), is slow on the timescale of the field frequency \( \omega_0 \), consid-
eration of the time dependent transport is simplified by invoking adiabatic assumption (treating $\vec{F}(t)$ as a parameter).

We start with Hamiltonian (1) in which interaction with driving field is written in the form presented in Eq. (4). Transforming the Hamiltonian into rotating frame of the field $\vec{F}$, we neglect non-diagonal terms, since they contribute to retarded (advanced) projection only and coupling to the bath is assumed to be small relative to coupling to the con-

\[ \hat{H} = e^S \hat{H} e^{-S} + \left( i \frac{\partial}{\partial t} e^S \right) e^{-S} \]  
\[ \hat{S} = -\frac{i \omega_0 t}{2} (\hat{n}_1 - \hat{n}_2) \]  

where $\hat{n}_i = d_i^\dagger d_i$ ($i = 1, 2$), leads to

\[ \hat{H} = \hat{H}_0 + \hat{V} \]
\[ \hat{H}_0 = \sum_{i=1,2} \varepsilon_i d_i^\dagger d_i - \left( \mu_{12} d_1^\dagger d_2 + \mu_{21} d_2^\dagger d_1 \right) \hat{F}(t) \]
\[ \hat{V} = \sum_{k \in \{L,R\}} \varepsilon_k c_k^\dagger c_k + \sum_{\alpha} \omega_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha \]

where

\[ \varepsilon_i = \varepsilon_i - (-1)^i \omega_0 / 2 \]

Within rotating wave approximation only diagonal elements of the self-energy due to coupling to the contacts (electron transfer) $\Sigma^{et}$, Eq. (9), and self-energy due to coupling to electron-hole excitations (energy transfer) $\Sigma^{en}$, Eq. (15), survive

\[ \Sigma^{et}_{ii}(\tau_1, \tau_2) = \Sigma^{et}_{ii}(\tau_1, \tau_2) e^{i(-1)^i \omega_0 (t_1 - t_2)/2} \]  
\[ \Sigma^{en}_{ii}(\tau_1, \tau_2) = \Sigma^{en}_{ii}(\tau_1, \tau_2) e^{i(-1)^i \omega_0 (t_1 - t_2)} \]

For self-energy due to coupling to photon bath $\Sigma^p$, Eq. (19), we neglect non-diagonal terms, since they contribute to retarded (advanced) projection only and coupling to the bath is assumed to be small relative to coupling to the contacts. The self-energy becomes diagonal

\[ \Sigma^{p}_{ii}(\tau_1, \tau_2) = \Sigma^{p}_{ii}(\tau_1, \tau_2) e^{i(-1)^i \omega_0 (t_1 - t_2)} \]

Resulting Green functions $\hat{G}(t_1, t_2)$ depend parametrically on slow time variable $t = (t_1 + t_2)/2$ through time dependence of the envelope $\hat{F}(t)$, Eq. (34). Transforming to Wigner coordinates, taking Fourier transform in the relative coordinate $t_1 - t_2$, and using gradient expansion leads to the following expressions for charge

\[ I_K(t) = \sum_{n=0}^{\infty} \frac{i^n}{2n!} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \]
\[ \text{Tr} \left[ \frac{\partial^n \Sigma^{K}_{ii}(E)}{\partial E^n} \frac{\partial^n \hat{G}^>(t, E)}{\partial t^n} - \frac{\partial^n \Sigma^{K}_{ii}(E)}{\partial E^n} \frac{\partial^n \hat{G}^<(t, E)}{\partial t^n} \right] \]

and photon

\[ \bar{J}_a(t) = \left| V^p_a \right|^2 \sum_{n,m=0}^{\infty} \frac{i^{n+m}}{2^{n+m} n! m!} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \]
\[ \left( \frac{\partial^n}{\partial t^n} \frac{\partial^n}{\partial E^n} G^{>}_{11}(t, E) \right) \left( \frac{\partial^m}{\partial t^m} \frac{\partial^m}{\partial E^m} G^{<}_{22}(t, E + \omega_a) \right) \]

fluxes. Eqs. (10) and (11) are main results of this section. They are to be compared with general expressions [5] and [20], respectively.

VI. NUMERICAL RESULTS

We calculate time-dependent transport and optical response by invoking Runge-Kutta scheme with adaptive stepsize control to solve numerically system of differential equations [20].

FIG. 1: (Color online) Current on the left, $I_L$, and right, $I_R$, interfaces vs. time for single level model. Numerical results (dashed line, red) are compared to analytical expression (solid line, blue). Also shown is sum of the currents, $I_L + I_R$ at the two interfaces (dotted line, black). See text for parameters.

To check accuracy of our numerical approach we start from a test calculation for a single level model. Analytical solution is available for the latter. In a biased junction ($\mu_L = 1$ eV and $\mu_R = -1$ eV) the level is set below both chemical potentials ($\varepsilon_0 = -2$ eV), so that initially the level is occupied and current through the junction is negligible (escape rates are $\Gamma_L = \Gamma_R = 0.2$). At time $t_0$ position of the level is shifted to 0 eV (steplike
modulation). Here and below we assume Fermi distributions in the leads corresponding to room temperature $T = 300$ K. Figure 1 presents transient current at the two interfaces (direction from contact into the system is taken to be positive for both currents) calculated numerically (dashed line) and with analytical solution (solid line). Also shown is sum of the currents at the two interfaces (dotted line). Outflux of electrons from initially fully populated level into the right contact leads to ringing effect. Eventually the current achieves steady-state. Our numerical procedure is seen to give good correspondence with the analytical result. Below we use similar parameters for calculation of time-dependent response of the two-level system.

We consider two geometries of a junction: a bowtie antenna like electrodes and electrodes in the form of metallic spheres. Large single-molecule fluorescence measurements were reported recently for the former.\cite{53} The latter (molecule between two metallic nanoparticles) is customary in experimental setups.\cite{54}

Both structures are excited by a plane wave polarized along the axis of symmetry (i.e. along the axis connecting centers of two spheres, for instance). The electric field amplitude is then detected as a function of time. Recorded amplitudes are Fourier transformed and normalized with respect to the incident field amplitude leading to enhancement as a function in the frequency domain.

Results of our simulations for both geometries are presented in Fig. 2 showing intensity enhancements in the main panel. As expected bowtie structures result in noticeably higher enhancements reaching 630 centered at $\lambda = 600$ nm for a bowtie antenna with a gap of 5 nm. Two spheres also show significant enhancement of 55 around $\lambda = 370$ nm. We note that the bowtie antenna in comparison to two spheres system exhibits two resonances. The “blue” resonance located at low wavelength corresponds to rod lightning effect with high enhancement localized primarily at the edges of each triangle. This feature disappears from the spectrum once sharp corners are replaced with smooth edges.\cite{42} Top and bottom insets show intensity enhancement distributions at resonant conditions for the two spheres and bowtie antennas, respectively. We place molecular junction in the hot spot regions.

Figure 3 shows time-dependent populations of molecular junction driven by external electromagnetic field for the ground, $n_1$, and excited, $n_2$, states. Time-dependent current at the left interface, $I_L$, is shown in Fig. 3b. Parameters of the calculation are $T = 300$ K, $\varepsilon_1 = -1$ eV, $\varepsilon_2 = 1$ eV, $|\Gamma_K|_{nm} = 0.1$ eV and $|\Gamma_K|_{12} = |\Gamma_K|_{21} = 0$.
are obtained for bowtie geometry with 10 nm gap at bias $V = 2$ V. Exact numerical calculation (solid line) is compared with adiabatic approximation data (dashed line). One sees, that the adiabatic approximation for realistic parameters provides qualitatively correct results. It misses however delay (memory) effects and overestimates response signal. Electromagnetic pulse depletes ground state and populates excited state, which for the chosen bias leads to increase of current through the junction due to increase in transmission of the excited state channel (see also Fig. 5 below).

We compare response of the two molecular junction geometries in Fig. 4. Bowtie geometry provides stronger local enhancement, and consequently stronger molecular response. In the case of spherical nanoparticles we consider two possible positions of molecule between the electrodes: symmetric and asymmetric (3 nm shift from the center, where the field enhancement for the geometry is strongest). These yield weakest and intermediate signal, respectively. Note, that it is natural to expect that local field enhancement is stronger for a structure with uneven surface. Fig. 4a presents time-dependent current for the three cases. Total optical response, Eq. (23), is shown in Fig. 4b. We choose $\eta = 5 \cdot 10^{-5}$ and $\omega_c = 2$ eV, other parameters are as in Fig. 3. Note much more sensitive character of optical response to resonant conditions. It results from our choice of $\gamma(\omega)$, Eq. (24), so that most of the electronic excitation contributes to current. While the choice is arbitrary, it indicates importance of the environment (bath spectral density). Fig. 4c shows time-dependent optical spectrum, Eq. (22), for the bowtie geometry. The signal follows (with a delay) the pulse of the external field. Asymmetric character of the spectrum relative to resonance, $\omega_c = 2$ eV, stems from overlap of Lorentzians (levels broadening due to coupling to the contacts) centered on ground and excited states.

![Figure 4](image4.png)

**FIG. 4:** (Color online) The two-level (HOMO-LUMO) model. Shown are (a) current and (b) total optical response, vs. time for bowtie nanoantennas (the strongest signal, blue) and two spheres junction geometries. In the latter case the response is calculated for two positions of the molecule in the junction: in the middle between the spheres (the weakest signal, red) and closer to one of the spheres (intermediate signal, (a) white silhouette and (b) solid line, black). Figure (c) shows contour map of optical flux, for bowtie geometry vs. outgoing frequency and time. See text for parameters.

$m = 1, 2$ and $K = L, R$. For interaction with electromagnetic field we take $\bar{\mu} \bar{E}_0 = 0.005$ eV, where $\bar{E}_0$ is amplitude of the external laser field before enhancement. Bias $V$ is applied symmetrically $\mu_{L,R} = E_F \pm eV/2$, and the Fermi energy is $E_F = 0$. Results presented in Fig. 4 are obtained for bowtie geometry with 10 nm gap at bias $V = 2$ V. Exact numerical calculation (solid line) is compared with adiabatic approximation data (dashed line). One sees, that the adiabatic approximation for realistic parameters provides qualitatively correct results. It misses however delay (memory) effects and overestimates response signal. Electromagnetic pulse depletes ground state and populates excited state, which for the chosen bias leads to increase of current through the junction due to increase in transmission of the excited state channel (see also Fig. 5 below).

We compare response of the two molecular junction geometries in Fig. 4. Bowtie geometry provides stronger local enhancement, and consequently stronger molecular response. In the case of spherical nanoparticles we consider two possible positions of molecule between the electrodes: symmetric and asymmetric (3 nm shift from the center, where the field enhancement for the geometry is strongest). These yield weakest and intermediate signal, respectively. Note, that it is natural to expect that local field enhancement is stronger for a structure with uneven surface. Fig. 4a presents time-dependent current for the three cases. Total optical response, Eq. (23), is shown in Fig. 4b. We choose $\eta = 5 \cdot 10^{-5}$ and $\omega_c = 2$ eV, other parameters are as in Fig. 3. Note much more sensitive character of optical response to resonant conditions. It results from our choice of $\gamma(\omega)$, Eq. (24), so that most of the electronic excitation contributes to current. While the choice is arbitrary, it indicates importance of the environment (bath spectral density). Fig. 4c shows time-dependent optical spectrum, Eq. (22), for the bowtie geometry. The signal follows (with a delay) the pulse of the external field. Asymmetric character of the spectrum relative to resonance, $\omega_c = 2$ eV, stems from overlap of Lorentzians (levels broadening due to coupling to the contacts) centered on ground and excited states.

![Figure 5](image5.png)

**FIG. 5:** (Color online) Current vs. time for the two-level (HOMO-LUMO) model calculated at two different biases. See text for parameters.
culation is done for bowtie geometry with a gap of 10 nm, parameters are the same as in Fig. 3. For pre-resonant bias, $V = 1.8$ V, optical excitation is effective in depleting the ground and populating the excited states of the molecule, which results in increased current through both channels. At post-resonant bias, $V = 2.2$ V, the charge transfer channels are open. Here optical excitation contributes mostly to decrease in conductance of the ground state and appearance of leakage current to the left contact in the excited state. This leads to overall decrease in current through the junction (see also discussion below).

![Graph showing total optical response vs. time with and without electron-hole excitations](image)

**FIG. 6:** (Color online) Role of energy transfer process. Shown are (a) total optical response vs. time with (dotted line, red) and without (solid line, blue) electron-hole excitations and (b) difference between current calculated with and without electron-hole excitations vs. time and bias. Calculations are performed within adiabatic approximation scheme. See text for parameters.

Calculations so far disregarded influence of both energy transfer, Eq. (5), and external photon bath, Eq. (6), (except its contribution to optical rate) on electronic distribution in the molecule. While the latter can indeed be disregarded due to smallness of the reasonable coupling parameter (see Ref. 37 for discussion), the former can make a difference. Here we illustrate influence of energy transfer process on time-dependent response of the junction within adiabatic approximation (full numeric calculation is straightforward but time-consuming). Figure 6 shows total optical response calculated with (dashed line) and without (solid line) energy transfer included. Calculation is done for bowtie geometry with 10 nm gap at pre-resonant constant bias $V = 1.8$ V. Other parameters are as in Fig. 3. As expected, energy transfer diminishes optical response of the junction, since both energy transfer from molecule to contacts and fluorescence compete for the same excess electronic population in the excited state. Current change upon including electron-hole excitations into consideration is more interesting. Interplay between channel blocking and resonant pathways for electron transfer may lead to increase in current through the junction as is illustrated in Fig. 6(b). This effect is similar to the situation presented in Fig. 5.

**VII. CONCLUSION**

We consider a two-level (HOMO-LUMO) model of molecular junction driven by external time-dependent laser field. Finite difference time domain technique is used to calculate field distribution for two junction geometries. Resulting local field at the molecule is considered to be the driving force. We assume that the junction is initially in a nonequilibrium steady-state resulting from applied constant bias. At time $t_0$ driving force (laser pulse) starts to influence the system. Time-dependent transport (charge flux through the junction) and optical response (photon flux from the molecule into accepting modes) are calculated for a set of geometries and applied biases. We rewrite a nonequilibrium Green function technique for time-dependent calculation in a form convenient for treating many-level molecular systems. Results of the simulations within the approach are compared to approximate scheme for an adiabatic pumping regime. Note that while our present consideration is restricted to driving force applied to the molecule only, generalization of the approach to situations of time-dependent bias and/or coupling between molecule and contacts is straightforward. Extension of the consideration to realistic molecular devices, taking into account time-dependent non-equilibrium distribution in the contacts and spatial profile of the field, and considering interplay of time-dependencies of bias and laser field are goals of future research.

**Acknowledgments**

M.S. is grateful to ASU financial and technical support (startup funds). M.G. gratefully acknowledges support by the UCSD (startup funds), the UC Academic Senate (research grant), and the U.S.-Israel Binational Science
