Nonstationary theory of magnetic field induced current for molecular spin nanojunction

M. Jouravlev\textsuperscript{1} and Kwang S. Kim\textsuperscript{2}

\textit{Center for Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea}

Abstract

For the study of molecular spin junctions, we take into account two types of couplings between the molecule and the metal leads: (i) electron transfer that gives rise to net current in the biased junction and (ii) energy transfer between the molecule and the leads. Using a rotating wave approximation in the Heisenberg representation, we derive a set of differential equations for the expectation values of relevant variables: electron and phonon populations and molecular polarization. A magnetic field control method to enhance the charge transfer at spin nanojunctions, which characterizes the molecule feature, is discussed. An approximate analytical solution of the resulting dynamical equation is supported by numerical solution. The magnetic control by charge transfer is described by transient pseudo-fermions of electrons interacting with spins. The rapid adiabatic passage of the energy between the molecule and the leads is taken into account. The current for molecular spin nanojunctions is derived.

PACS numbers: 73.63.Rt, 73.23.Hk, 85.65+h

\textsuperscript{*}Electronic address: 1) mikhail@postech.ac.kr, 2) kim@postech.ac.kr
I. INTRODUCTION

A molecular spin nanojunction is a nanodevice where the electron transfer depends on the spin state of electrons passing through the molecule and is controlled by an external magnetic field. The giant magnetoresistance\(^1\), \(2, 3, 4\) and tunneling magnetoresistance\(^5, 6, 7\) are widely used as molecular memory devices for magnetic field recording, and this has launched a new field of nanoelectronics - "spintronics". Recently, even super magnetoresistance has been discussed through graphene nanoribbons\(^8\).

The main theoretical principle to describe the properties of tunneling electron transfer was first proposed by Gamov\(^9\). In the last few years some theoretical and computational aspects of electron conduction in nanojunctions have been under intense study\(^10, 11, 12, 13, 14\). The electric-field driven magnetic switching has been discussed\(^15\) and the light induced switching behavior in the conduction properties of molecular nanojunctions has been demonstrated\(^16, 17, 18, 19, 20\). The formalism of the quantized electron conductance was derived\(^21, 22\) and the conduction behavior in the heterostructure of molecular nanojunction was formulated. The spin nanojunction for carbon nanotubes or graphene nanoribbons was investigated\(^23, 24\). Spin dependent electron transport was seen in electron nanotubes and graphene excited by nonstationary magnetic field\(^25\) as well as in graphene nanoribbons doped by chemically active impurities\(^26, 27\).

The formalism of the current in molecular nanojunctions was derived based on elastic electron scattering between two electronic baths corresponding to two leads\(^28, 29, 30\). In the elastic scattering limit, energy is lost in the lower potential lead, while no energy dissipation occurs in the molecular nanojunction. Following the Landauer formalism\(^21, 22, 31, 32\), most of theoretical works on the nanojunction transport were done within a scattering theory approach, which neglects the contact problems and the influence of the scattering channels as well as the mutual influences between the electron and phonon subsystems\(^33, 34, 35\).

The electron transfer rate in terms of the coupling between the electronic state and the nuclear vibration was provided\(^36\). The spatial resolution at the atomic scale for single molecules adsorbed on the surface has also been achieved by scanning tunneling microscopy (STM)\(^37\). The nuclear vibration is described by transversal time or contact time for the electron transfer through a molecule. In order to estimate the transversal time, it is necessary
to take into account the chain length of a molecule in a small gap between two leads. The transfer time can be long enough to be comparable to the molecular vibration period. The strong coupling between molecular vibration and electronic states could result in trapping of electrons and transition from the coherent to incoherent state. This transition has been found in molecular nanowires under the radiation field. It could be achieved by both long range electron transfers and currents through the molecular nanojunctions in nonequilibrium states. A class of molecules characterized by strong charge-transfer driven transitions into their first excited state has been investigated. The dipole moment of such molecules changes considerably upon the excitation, resulting in a substantial electronic charge redistribution.

Here, we focus our attention on the transport of the electron through the single-molecule spin nanojunction under the external magnetic field which controls a small nanogap between two metal leads. This research effort is now devoted to extending the spin-dependent effects to magnetic molecular nanojunction for spintronic nanodevices with relatively strong electron-phonon coupling and large spin coherence. We investigate the spin polarized electron transport in either occupied (OMO) or unoccupied molecular orbitals (UMO), (Fig. 1). For a molecular spin nanojunction connecting between two metal leads, time dependent magnetic fields can create an internal driving force for the charge to flow between the two leads. We suppose that the molecular junction has extremely weak spin-orbit interaction and weak hyper-fine interaction, meaning that the electron spin diffusion length is long enough to provide the spin-polarized electron injection and the spin transport between the leads. Our objective in the present work is to extend the theory of Galperin, Fainberg and Nitzan to the case including magnetic fields and to apply the theory to the study of coherent control of nanojunction transport. While these problems are of general and fundamental interest, we note that this study is related to the efforts to develop novel single-electron devices, magnetic memory devices, and single-electron transistors with magnetic gating. In addition, the potential significance of molecular spin nanojunctions for device applications lies in the possibility of creating magnetic switches that could be incorporated in future generations of communication systems. It is conceivable that these devices will employ coherent spin manipulations for quantum information processing.

In this study we particularly develop theory for the effects of strong electron-phonon interactions on tunnelling nanojunction and inelastic tunnelling in quantum point contacts.
associated with the non-linear conduction phenomena. There are reasons to consider molecular nanojunctions subjected to strong magnetic fields. First, the structure of such junctions is compatible with the configuration considered for high electromagnetic field as in tip-enhanced scanning near field optical microscopy (SNOM)\[43\]. Second, consideration of the spin nanojunction stability suggests that strong radiation fields should be applied in the sequence of well separated pulses to allow for sufficient relaxation and heat dissipation. Finally, consideration of strong time dependent pulses makes it possible to study the way to optimize the desired effect for the magnetic field induced electron tunneling, i.e. to explore the possibility for coherent control of charge flow between the leads.

This paper is organized as follows. Sec.II introduces our model. Sec.III derives a closed set of Heisenberg equations for the average values for the magnetic spin operators and for the annihilation and creation operators for the electrons in the molecular states. In Sec. IV and V we derive the current functions for the magnetic spin operators and the formulas for the current and charge transfer during the magnetic pulse action, and calculate the current induced by a quasi-stationary magnetic pulse. The results for control of the current and the transferred charge by chirped pulses are summarized in Sec.VI, and the conclusion is made in Sec.VII. In Appendices, we show that in the absence of the radiative and nonradiative energy transfer couplings, the equations of motion derived here lead to the well known Landauer’s type formula for the current.

II. HAMILTONIAN

As for the simplest theoretical view of an efficient spin molecular transport system, the actual contacts of the molecule to both electrodes are presented in Fig.1. The metal electrodes are on the left (L) and right (R) sides. The occupied molecular orbitals (OMO) and unoccupied molecular orbitals (UMO) are presented by line segments, and the spins are depicted by arrows. A molecule is positioned between two leads represented by free electron reservoirs L and R. The system interacts with the magnetic field. The reservoirs are characterized by the electronic chemical potentials \(\mu_L\) and \(\mu_R\), where the difference \(\mu_L - \mu_R = eV\) is the imposed voltage bias. The coupling \(\Gamma\) is shown by double headed arrows. In the independent electron picture, the transition between the ground and excited molecular states corresponds to the transfer of an electron between OMO and UMO levels. There
FIG. 1: A model for the molecule-electrode junction. The electronic structure is substantially modified as the molecule is between two leads by a nanojunction. The right ($R = \{|r\}\rangle$) and left ($L = \{|l\}\rangle$) manifolds represent two metal leads characterized by electrochemical potentials $\mu_R$ and $\mu_L$, respectively. Occupied molecular orbitals (OMO) and unoccupied molecular orbitals (UMO) are schematically drawn. The Fermi energy of the left electrode ($E_{FL}$) is higher than the Fermi energy of the right electrode ($E_{FR}$) in the presence of magnetic field. In the Hamiltonians Eqs. (2, 4, and 5), indices $k, k'$ denote the states of the metal leads, and indices $m, m'$ denote the states of the molecule. Couplings $\Gamma_L$ and $\Gamma_R$ are denoted by double headed arrows.

are couplings between atomic levels and electrodes. The Fermi level of the electrodes lies within the gap between the highest OMO (HOMO) and the lowest UMO (LUMO) of the molecule. This picture assumes that the coupling between a molecule and an electrode is relatively weak compared with the interatomic interactions. The magnetization direction is either parallel or perpendicular to the external magnetic field $B(r, t)$. In Fig. 1 the model Hamiltonian Eq. (1) consists of the unperturbed part ($\hat{H}_0$), the perturbed part ($\hat{V}$), and the magnetic field effect part ($\hat{H}_B$):

$$\hat{H} = \hat{H}_0 + \hat{H}_B + \hat{V}, \quad (1)$$
where

\[
\hat{H}_0 = \sum_{\alpha} \omega_{\alpha} \hat{a}^+_\alpha \hat{a}_\alpha + \sum_{\beta} \omega_{\beta} \hat{b}^+_\beta \hat{b}_\beta \\
+ \sum_{m \in M, \sigma} \varepsilon_m \hat{c}^+_{m,\sigma} \hat{c}_{m,\sigma} + \sum_{k \in \{L, R\}, \sigma} \varepsilon_k \hat{c}^+_{k,\sigma} \hat{c}_{k,\sigma}.
\]  

(2)

Here, \(L\) and \(R\) denote the left and right leads, respectively. We use \(\hbar = 1\) and \(e = 1\) here and below. The Hamiltonian \(\hat{H}_0\) (Eq. (2)) contains additive terms that correspond to the isolated molecule (index: \(m\)) and the free leads (index: \(k\)). Operators \(\hat{c}_{m,\sigma}\) (\(\hat{c}^+_{m,\sigma}\)) and \(\hat{c}_{k,\sigma}\) (\(\hat{c}^+_{k,\sigma}\)) are an annihilation (creation) operator of an electron in the molecule and that in the leads, respectively, where \(\sigma\) is the spin (\(\uparrow\) or \(\downarrow\)). Operators \(\hat{a}_\alpha\) (\(\hat{a}^+_\alpha\)) and \(\hat{b}_\beta\) (\(\hat{b}^+_\beta\)) are an annihilation (creation) operator of a phonon in the molecule and that in the thermal bath or phonon reservoir, respectively. The interaction part \(\hat{V}\) of Hamiltonian (Eq. (1)) is:

\[
\hat{V} = \hat{V}_M + \hat{V}_N + \hat{V}_V.
\]  

(3)

Here the \(\hat{V}_M\) term describes the coupling between the molecular electronic subsystem and the free-electron reservoirs in the leads, and \(\hat{V}_M\) has the form [44]:

\[
\hat{V}_M = \sum_{K=L, R} \sum_{m \in M; k \in K, \sigma} (V^{(MK)}_{km}) \hat{c}^+_{k,\sigma} \hat{c}_{m,\sigma} + \text{h.c.).}
\]  

(4)

Here h.c. denotes Hermitian conjugate. The term \(\hat{V}_N\) of the Hamiltonian (Eq. (3)) describes the energy transfer between the molecule and the leads. It is written in the form of Anderson Hamiltonian [44, 45, 46]:

\[
\hat{V}_N = \sum_{K=L, R} \sum_{m \neq m' \in M; k \neq k' \in K, \sigma} (V^{(NK)}_{kk'}) \hat{c}^+_{k',\sigma} \hat{c}_{k,\sigma} \hat{c}^+_{m',\sigma} \hat{c}_{m,\sigma} + \text{h.c.).}
\]  

(5)

Electrons of the nanojunction are coupled to both the vibrations of the molecule and the electrons of the leads. The \(\hat{V}_V\) term is the coupling potential of the interaction between electrons in the molecule and phonons in the subsystem, which is taken to be linear to the vibrational displacements in the form of Fröhlich Hamiltonian [46]:

\[
\hat{V}_V = \sum_{m \neq m' \in M, \sigma} (V^{(VK)}_{mm'}) \hat{c}^+_{m,\sigma} \hat{Q}^a_{\alpha} \hat{c}_{m',\sigma} + \text{h.c.).}
\]  

(6)

Here, \(\hat{Q}^a_{\alpha}\) is the vibrational displacement operator: \(\hat{Q}^a_{\alpha} = \hat{a}_\alpha + \hat{a}^+_\alpha\). Magnetic interactions in the Heisenberg model are employed as effective interactions between the spin of the electron
and the magnetic fields. The model of spin Hamiltonian is described by magnetic interactions with a few model parameters such as spin-spin interaction:

$$\hat{H}_S = -2 \sum_{m,m'} J_{m,m'} S_m S_{m'},$$  \hspace{1cm} (7)$$

which is called Ising spin Hamiltonian. Here, $S_m$ is the localized spin magnetic moment, $J_{m,m'}$ is the interaction potential for which each pair of spins $S_m$ and $S_{m'}$ is counted only once. $J_{m,m'}$ is the form of Green functions consistent with the spin fluctuation theory based on Kohn-Sham eigenfunctions. However it is dropped out because it is a constant independent of the magnetic field. The Hamiltonian has the form of Zeeman term with the external magnetic field $B(r, t)$ for the chosen value of the g-factor with the pseudo-Fermion operators:

$$\hat{H}_B = \textbf{H}_B(r, t) \hat{c}^+_{m, \sigma} \hat{c}_{m', \sigma'},$$  \hspace{1cm} (8)$$

where

$$\textbf{H}_B(r, t) = g \mu_B \sum_{m \in M, \sigma} \textbf{B}(r, t) S_m.$$  \hspace{1cm} (9)$$

Here, $g$ is the Lande g-factor which is normally close to 2; $\mu_B$ is the Bohr magneton and $B(r, t)$ is the magnetic field. The $\hat{c}^+_{m, \sigma}$ and $\hat{c}_{m, \sigma}$ operators describe pseudo-Fermion operators specified by $\sigma$ which raise the energies by $\pm g \mu_B B(r, t)$. Taking into account that electrons with the pseudo-Fermion properties exist only in the presence of the magnetic fields, we omit the index $\sigma$ in all formulas below.

### III. HEISENBERG EQUATIONS

The physics of the system can be described by different approaches. One is the method of nonequilibrium Green’s functions. It has advantages in formal treatment due to a diagrammatic representation, and it is particularly well suited for stationary processes where the Dyson equation can be cast in the energy representation. For time-dependent processes, a method based on the Heisenberg equations of motion for the expectation values of the operators provides a more transparent approach, since the quantities are more directly related to physical observables. Such a method is adopted here. The Heisenberg equations for $\hat{c}_m (\hat{c}_m^+)$ and $\hat{c}_k (\hat{c}_k^+)$ can be written as follows:

$$\frac{d\hat{c}_m}{dt} = \frac{i}{\hbar} [\hat{H}_0 + \hat{H}_B + \hat{V}_M + \hat{V}_N + \hat{V}_V, \hat{c}_m],$$  \hspace{1cm} (10)$$
\[
\frac{d \hat{c}_m}{dt} = \frac{i}{\hbar} [\hat{H}_0, \hat{c}_m] + \frac{i}{\hbar} [\hat{H}_B, \hat{c}_m] + \frac{i}{\hbar} [\hat{V}_M, \hat{c}_m] + \frac{i}{\hbar} [\hat{V}_N, \hat{c}_m] + \frac{i}{\hbar} [\hat{V}_V, \hat{c}_m]. 
\]

The equation of motion derived by the mathematical transformation is presented in Appendices \textit{A} and \textit{E}.

\[
\frac{d \hat{c}_m}{dt} = -\frac{i}{\hbar} \varepsilon_m \hat{c}_m - \frac{i}{\hbar} \sum_{K=L,R} \sum_{k \in K} V^{(MK)}_{mk} \hat{c}_k - \frac{i}{\hbar} \sum_{K=L,R} \sum_{k \neq k'} \{ V^{(NK)}_{kk'} \hat{c}_k \hat{c}_{k'} \delta_{2m} + V^{(NK)}_{kk'} \delta_{1m} \hat{c}_k \hat{c}_{k'} \} - \frac{i}{\hbar} \sum_{m \neq m' \in M} (V^{(VK)}_{mm'} \hat{Q}_a) \hat{c}_m + \frac{i}{\hbar} \hat{B}(r, t) \hat{c}_{m'} = (12)
\]

and

\[
\frac{d \hat{c}_m^+}{dt} = \frac{i}{\hbar} \varepsilon_m \hat{c}_m^+ + \frac{i}{\hbar} \sum_{K=L,R} \sum_{k \in K} V^{(MK)}_{km} \hat{c}_k^+ + \frac{i}{\hbar} \sum_{K=L,R} \sum_{k \neq k'} \{ V^{(NK)}_{kk'} \hat{c}_k^+ \hat{c}_{k'} \delta_{2m} + V^{(NK)}_{kk'} \delta_{1m} \hat{c}_k^+ \hat{c}_{k'} \} - \frac{i}{\hbar} \sum_{m \neq m' \in M} (V^{(VK)}_{mm'} \hat{Q}_a) \hat{c}_m^+ - \frac{i}{\hbar} \hat{B}(r, t) \hat{c}_{m'} = (13)
\]

\textbf{A. Calculation of electron transfer without external field}

We calculate the second term on the right-hand side of Eqs. (12) and (13). To do this, we shall write down the Heisenberg equation for \( \hat{c}_k \), when \( \hat{V}_N \) and \( \hat{V}_V \) terms are not included:

\[
\frac{d \hat{c}_k}{dt} = \frac{i}{\hbar} [\hat{H}_0, \hat{c}_k] + \frac{i}{\hbar} [\hat{V}_M, \hat{c}_k] 
\]

or

\[
\frac{d \hat{c}_k}{dt} = -\frac{i}{\hbar} \varepsilon_k \hat{c}_k - \frac{i}{\hbar} \sum_{m' \in M} V^{(MK)}_{km'} \hat{c}_{m'}  
\]

and

\[
\frac{d \hat{c}_m}{dt} = -\frac{i}{\hbar} \varepsilon_m \hat{c}_m - \frac{i}{\hbar} \sum_{k' \in K} V^{(MK)}_{km'} \hat{c}_{k'}  
\]

Since \( \frac{d}{dt}(\hat{c}_k \hat{c}_m) = \frac{d \hat{c}_k}{dt} \hat{c}_m + \hat{c}_k \frac{d \hat{c}_m}{dt} \), we obtain

\[
\frac{d \hat{c}_k^+ \hat{c}_m}{dt} = \frac{i}{\hbar} \varepsilon_k \hat{c}_k^+ \hat{c}_m + \frac{i}{\hbar} \sum_{m' \in M} V^{(MK)}_{m'k} \hat{c}_m^+ \hat{c}_m. 
\]
and
\[
\hat{c}_k \frac{d\hat{c}_m}{dt} = -\frac{i}{\hbar} \varepsilon_m \hat{c}_m + \frac{i}{\hbar} \sum_{K=L,R} \sum_{k' \in K} V_{mk'}^{(MK)} \hat{c}_m \hat{c}_{k'}.
\]

Then
\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_m \rangle = \frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \langle \hat{c}_k^+ \hat{c}_m \rangle + \frac{i}{\hbar} \sum_{m' \in M} V_{m'k}^{(MK)} \langle \hat{c}_m^+ \hat{c}_m \rangle - \frac{i}{\hbar} \sum_{K=L,R} \sum_{k' \in K} V_{mk'}^{(MK)} \langle \hat{c}_k^+ \hat{c}_{k'} \rangle
\]
\[(19)\]

where \(\langle ... \rangle\) denotes the averaging. Here we used \(\langle \hat{c}_m^+ \hat{c}_m \rangle = \langle \hat{c}_m^+ \hat{c}_m \rangle \delta_{mm'}\) in the second term on the right-hand side of Eq.\(19\) because of the following reasons. First, Eq.\(19\) was obtained by neglecting \(\hat{V}_N\) when the polarization \(\langle \hat{c}_m^+ \hat{c}_m \rangle |_{m \neq m'} = 0\). Second, the term \(\langle \hat{c}_m^+ \hat{c}_m \rangle |_{m \neq m'}\) is the non-resonant case. As to \(\langle \hat{c}_k^+ \hat{c}_{k'} \rangle\), this term is equal to
\[
\langle \hat{c}_k^+ \hat{c}_{k'} \rangle = f_K(\varepsilon_k) \delta_{kk'},
\]
\[(20)\]

where \(f_K(E) = [\exp((E - \mu_K)/k_B T) + 1]^{-1}\) is the Fermi function, \(E\) is the energy, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature. Using \(\langle \hat{c}_m^+ \hat{c}_m \rangle = \langle \hat{c}_m^+ \hat{c}_m \rangle \delta_{mm'} \equiv n_m\) and Eq.\(20\) for Eq.\(19\), we obtain
\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_m \rangle = \frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \langle \hat{c}_k^+ \hat{c}_m \rangle + \frac{i}{\hbar} V_{m'k}^{(MK)} [n_m - f_K(\varepsilon_k)].
\]
\[(21)\]

By integrating Eq.\(21\), we obtain
\[
\langle \hat{c}_k^+ \hat{c}_m \rangle = \frac{i}{\hbar} V_{m'k}^{(MK)} \int_0^t dt' \exp[i(\varepsilon_k - \varepsilon_m)(t - t')] [n_m(t') - f_K(\varepsilon_k)].
\]
\[(22)\]

By using the formula
\[
\int_0^\infty d\tau \exp[i(\varepsilon_k - \varepsilon_m)\tau] = \frac{ihP}{\varepsilon_k - \varepsilon_m} + \pi \frac{\delta(\varepsilon_k - \varepsilon_m)}{\varepsilon_k - \varepsilon_m},
\]
\[(23)\]

where \(P\) denotes the principal value and by assuming that the term \([n_m(t') - f_K(\varepsilon_k)]\) is slowly varying as compared to the exponential function, we can move the term outside the integral of \(\text{Eq.}21\). The resulting integral gives
$$\langle \hat{c}_k^\dagger \hat{c}_m \rangle \simeq \frac{i}{\hbar} V_{mk}^{(MK)}[n_m(t) - f_K(\varepsilon_k)] \int_0^\infty d\tau \exp\left[\frac{i}{\hbar}(\varepsilon_k - \varepsilon_m)\tau\right]$$

$$= \frac{i}{\hbar} V_{mk}^{(MK)}[n_m(t) - f_K(\varepsilon_k)] \left[\frac{i\hbar P}{\varepsilon_k - \varepsilon_m} + \hbar \pi \delta(\varepsilon_k - \varepsilon_m)\right].$$

Let us show the important result of the simplified equations for the current $I$. Taking into account only $\hat{V}_M$ ($V_{mk}^{(MK)}$) in Eq. (24), and substituting the last result into

$$\frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \in K} V_{km}^{(MK)} \langle \hat{c}_k^\dagger \hat{c}_m \rangle,$$

we have

$$\frac{2}{\hbar} \text{Im} \sum_{K=L,R} \sum_{k \in K} V_{km}^{(MK)} \langle \hat{c}_k^\dagger \hat{c}_m \rangle = \frac{2\pi}{\hbar} \sum_{K=L,R} \sum_{k \in K} |V_{km}^{(MK)}|^2 [n_m(t) - f_K(\varepsilon_k)] \delta(\varepsilon_k - \varepsilon_m)$$

$$= \sum_{K=L,R} [n_m(t) - f_K(\varepsilon_m)] \Gamma_{MK,m}. \quad (25)$$

where

$$\Gamma_{MK,m} = \frac{2\pi}{\hbar} \sum_{k \in K} |V_{km}^{(MK)}|^2 \delta(\varepsilon_k - \varepsilon_m). \quad (26)$$

Here we use the formula for current $I$, derived from well known definitions of the molecular nanojunction current presented in Refs. [30, 41, 55]

$$I = e \frac{d}{dt} \sum_{k \in L} \langle \hat{c}_k^\dagger \hat{c}_k \rangle = \frac{ie}{\hbar} \sum_{m=1,2} \sum_{k \in L} \langle V_{mk}^{(MK)} \hat{c}_m^\dagger \hat{c}_k - \text{h.c.} \rangle$$

$$= -\frac{2e}{\hbar} \text{Im} \sum_{m=1,2} \sum_{k \in L} V_{mk}^{(MK)} \langle \hat{c}_k^\dagger \hat{c}_m \rangle. \quad (27)$$

Taking into account that $\langle \hat{c}_m^\dagger \hat{c}_k \rangle = \langle \hat{c}_k^\dagger \hat{c}_m \rangle^*$, substituting Eq. (24) into Eq. (27), and using Eqs. (25) and (26), we have

$$I = -\frac{2e}{\hbar} \text{Im} \sum_{m=1,2} \sum_{k \in L} V_{mk}^{(MK)} \langle \hat{c}_k^\dagger \hat{c}_m \rangle^*$$

$$= e \sum_{m=1,2} \frac{2\pi}{\hbar} \sum_{k \in L} |V_{mk}^{(MK)}|^2 [n_m - f_L(\varepsilon_k)] \delta(\varepsilon_k - \varepsilon_m)$$

$$= e \sum_{m=1,2} [n_m - f_L(\varepsilon_m)] \Gamma_{ML,m}. \quad (28)$$
B. Calculation of energy transfer

We now compute the equations of motion for the relaxation induced by the molecule-metal lead couplings, \( \hat{V}_M \) and \( \hat{V}_N \). We assume that the relaxation processes due to \( \hat{V}_M \) and \( \hat{V}_N \) are not independent and also do not depend on the external magnetic field. Employing a Markovian approximation for the relaxation induced by the molecule-metal leads coupling, we derive a closed set of equations for the expectation values of binary function of the electron number operator in the molecule: \( \hat{n}_m = \hat{c}_m^+ \hat{c}_m \) or \( n_m \equiv \langle \hat{n}_m \rangle \), where \( n_m \) is the population of electrons in molecular state \( m \). The polarization operator in the molecule is \( \hat{b}_m = \hat{c}_m^+ \hat{c}_{m'} \), \( m \neq m' \) and the polarization of the molecule is \( p_M = \langle \hat{b}_m \rangle \) and \( p_M^+ = \langle \hat{b}_m^+ \rangle \). The molecular excitation population is \( \hat{b}_{kk'} = \hat{c}_k^+ \hat{c}_{k'} \). From now on, in our derivation we will consider only the HOMO (\(|1\rangle\)) and LUMO (\(|2\rangle\)) among OMO’s (\(|m\rangle\)) and UMO’s (\(|m'\rangle\)), respectively, for simplicity, while we may introduce \(|1\rangle = \sum_{m \in M} \rho_m |m\rangle\), and \(|2\rangle = \sum_{m' \in M} \rho_{m'} |m'\rangle\), where \( \rho_m (\rho_{m'}) \) is the density of the electron level \( m (m') \) of the molecule\(^{27}\). The derivation could be more general so that all OMOs and UMOs might be considered. In the case of only HOMO and LUMO, \( \hat{c}_m (\hat{c}_m^+) \) and \( \hat{c}_{m'} (\hat{c}_{m'}^+) \) will be simply replaced respectively by \( \hat{c}_1 (\hat{c}_1^+) \) and \( \hat{c}_2 (\hat{c}_2^+) \) variables of the annihilation (creation) operators for electrons in molecular states \(|1\rangle\) and \(|2\rangle\)\(^{28,29,41}\). In the next formulas we shall use the notations made in Ref.\(^{41}\). The equations of motion in Eq.\((12)\) and Eq.\((13)\) include couplings of additional correlations of the second order \( \langle \hat{b}_{mk} \rangle \) due to the electron-transfer interaction \( \hat{V}_M \) and higher-order correlations \( \hat{b}_M \hat{b}_{kk'} \) due to the energy transfer \( \hat{V}_N \). Introducing the following notation: \( \hat{b}_M^+ = \hat{c}_2^+ \hat{c}_1, \hat{b}_M = \hat{c}_1^+ \hat{c}_2, \hat{b}_{kk'}^+ = \hat{b}_{kk'}^+ = \hat{c}_k^+ \hat{c}_{k'}, \hat{b}_{kk'} = \hat{b}_{kk'} = \hat{c}_k^+ \hat{c}_k \), and taking into account \( \langle \hat{b}_{kk'}^+ \rangle = \langle \hat{b}_{kk'} \rangle = f_k (\varepsilon_k) \delta_{kk'} \), we can write: \( \hat{c}_1^+ \hat{c}_{kk'} \hat{c}_2 = \hat{c}_1^+ \hat{c}_{k} \hat{c}_k^+ \hat{c}_{k'} = \hat{b}_M \hat{b}_{kk'} \). Then, \( \hat{V}_N \) (Eq.\((5)\)) is represented as

\[
\hat{V}_N = \sum_{K=L,R} \sum_{k' \neq k'' \in K} (V_{k''k}^{(NK)} \hat{b}_{k''k} + V_{k''k}^{(NK)} \hat{b}_{k''k}^+). \tag{29}
\]

From the Heisenberg equation Eq.\((10)\), we have

\[
\frac{d}{dt} \hat{b}_M \hat{b}_{kk'}^+ = \frac{i}{\hbar} \left[ \sum_{m=1,2} \varepsilon_m \hat{n}_m + \sum_{k'' \in \{L,R\}} \varepsilon_{k''k} \hat{n}_{k''} \hat{b}_M \hat{b}_{kk'}^+ \right] + \frac{i}{\hbar} [\hat{V}_N, \hat{b}_M \hat{b}_{kk'}^+]. \tag{30}
\]
The bilinear product of Fermion or pseudo-Fermion operators for \( \hat{a}_i \) commutes with the bilinear product of Fermion operators for any function \( \hat{f}_j \), where \( i \neq j \). For \( i \neq j \),
\[
[\hat{a}_i, \hat{f}_j] = \hat{a}_i \hat{f}_j - \hat{f}_j \hat{a}_i \right] = 0, \quad [\hat{n}_m, \hat{b}_M \hat{b}_{k'k}] = \hat{n}_m \hat{b}_M \hat{b}_{k'k} - \hat{b}_M \hat{b}_{k'k} \hat{n}_m = [\hat{n}_m, \hat{b}_M] \hat{b}_{k'k}, \quad \text{and}
\]
\[
[\hat{n}_m, \hat{b}_M] = [\hat{c}_m^+ \hat{c}_m, \hat{c}_1^+ \hat{c}_2] = (-1)^{m-1} \hat{b}_M (1 - 2 \hat{n}_m). \quad \text{For the Poisson brackets for the bilinear products of the Fermion operators, we have}
\]
\[
[\hat{V}_N, \hat{b}_M \hat{b}_{k'k'}] = -\frac{i}{\hbar} \sum_{K=L,R} \sum_{k \neq k' \in K} V_{k'k}^{(NK)} \hat{b}_{k,k'} \hat{b}_{k'k'} (\hat{b}_M \hat{b}_{k'k} - \hat{b}_M \hat{b}_{k'k})
\]
\[
= \frac{i}{\hbar} \sum_{K'} \sum_{k' \neq k' \in K'} V_{k'k'}^{(NK)} \hat{b}_{k,k'} \hat{b}_{k'k'} (\sum_{m \neq m' \in M} \hat{n}_m - 1). \quad (31)
\]

IV. CALCULATION OF CURRENT

The simplest approach of transport in a molecular spin nanojunction is to assume that incoming electrons are scattered both at the noble metal-molecule interfaces and along the molecular chains. Then, the conductance will depend on the net probability of scattering \[39\]. Elastic scattering does not forbid electrons to transport through the nanojunction. The coherent conductance takes place in most molecular chains and nanowires when the electron transport occurs far from a resonance frequency between the metal Fermi energy and the molecular eigenstates at low temperatures \[39\]. Landauer theory assumes that electrons move smoothly from one electrode (\( L \)) to another (\( R \)) only by elastic scattering within nanojunction. In the presence of magnetic impurities or ferromagnetic leads, electrons would show the spin dependent transport ("spin valve behavior") in the presence of magnetic field. The spin polarized electron current emission is excited by magnetic field between metal leads. Thus, we take into account the linear form of new spin electron polarization added in the Landauer formalism. The total current \( I \) is taken by the rate of change of occupation number operator of electrons in the molecule is described in \[30, 41, 55\]. In Eq. (27), the current \( I \) represents the rate of flow of electrons from the left electrode to the molecule. thus using the previous results for \( \langle c_k^+ c_m \rangle \) we obtain
Summing Eq. (32) and (33) and taking the expectation values, we have:

\[
\frac{d\hat{c}_k^+}{dt} \hat{c}_m = \frac{i}{\hbar} \varepsilon_k \hat{c}_k^+ \hat{c}_m + \frac{i}{\hbar} \sum_{K=L,R,k \in K} V_{km}^{(MK)} \hat{c}_k^+ \hat{c}_m + \frac{i}{\hbar} \sum_{K=L,R,k \in K} \{ V_{(MK)k',k} \hat{c}_1^+ \hat{c}_k \hat{c}_m + V_{(MK)k,k} \hat{c}_k^+ \hat{c}_k \hat{c}_m \} \tag{32}
\]

\[
\hat{c}_k^+ \frac{d\hat{c}_m}{dt} = -\frac{i}{\hbar} \varepsilon_m \hat{c}_k^+ \hat{c}_m - \frac{i}{\hbar} \sum_{K=L,R,k \in K} V_{mk}^{(MK)} \hat{c}_m \hat{c}_k + \frac{i}{\hbar} \sum_{K=L,R,k \in K} V_{mk'}^{(MK)} \hat{c}_k \hat{c}_m' - \frac{i}{\hbar} \sum_{K=L,R,k \in K} \{ V_{(MK)k,k'} \delta_{2m} \hat{c}_k^+ \hat{c}_k \hat{c}_m + V_{(MK)k',k} \delta_{1m} \hat{c}_m \hat{c}_k \hat{c}_k' \} - \frac{i}{\hbar} \sum_{m \neq m' \in M} V_{mm'}^{(VK)} (\hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m) \tag{33}
\]

Summing Eq. (32) and (33) and taking the expectation values, we have:

\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_m \rangle = \frac{i}{\hbar} (\varepsilon_k - \varepsilon_n) \langle \hat{c}_k^+ \hat{c}_m \rangle + \frac{i}{\hbar} \sum_{m \in M} \langle \hat{c}_m \rangle \langle \hat{c}_m \rangle - \frac{i}{\hbar} \sum_{K=L,R,k \in K} \langle \hat{c}_k \hat{c}_k \rangle + \frac{i}{\hbar} \sum_{k \in K} \langle \hat{c}_k \hat{c}_k \rangle - \frac{i}{\hbar} \sum_{k \in K} \langle \hat{c}_k \rangle \langle \hat{c}_k \rangle - \frac{i}{\hbar} \sum_{m \neq m' \in M} \sum_{k \in L} V_{mm'}^{(VK)} (\hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m) \tag{34}
\]

for the current we have from Eq. (27) and by full analogy with Eqs. (33) and (34), we obtain a general formula for the total current given by the rate of change of the occupation number operator of electrons in the molecule.

\[
I = \frac{ie}{\hbar} \sum_{m \in M} \sum_{k \in L} \langle \hat{V}^{(MK)}_{m'k} \hat{c}_m^+ \hat{c}_k \rangle - \langle \text{h.c.} \rangle + \frac{ie}{\hbar} \left\{ \sum_{k \in L} \sum_{k' \neq k \in L} \langle \hat{V}^{(NK)}_{k'k} \hat{c}_k^+ \hat{c}_1 + \hat{c}_1^+ \hat{c}_k \rangle \hat{c}_k \right\} - \sum_{k \in L} \sum_{k' \neq k \in L} \langle \hat{V}^{(NK)}_{kk'} \hat{c}_k^+ \hat{c}_1 + \hat{c}_1^+ \hat{c}_k \rangle \hat{c}_k' \right\} + \frac{i}{\hbar} \sum_{k \in L} \langle \hat{H}_B (\text{r}, t) \rangle \langle \hat{c}_k^+ \hat{c}_m \rangle - \frac{ie}{\hbar} \sum_{m \neq m' \in M} \sum_{k \in L} V^{VK}_{mm'} \langle \hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m \rangle + \langle \hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m \rangle \tag{35}
\]
Here, the energy transfer, the electron-phonon interaction as well as the external magnetic field effect is included. The term in the braces on the right-hand side of the last equation is equal to zero. This can be seen if we exchange $k \leftrightarrow k'$ in the second term of the braces. From Eq. (35) one would select the part of current excited by magnetic field by using Eqs. (24-28). We have a simplified form for the current:

$$I_H = \frac{ie}{\hbar} H_B(r, t) \sum_{m \in M} [n_m - f_K(\varepsilon_k)] \Gamma_{ML,m}. \quad (36)$$

For the Hamiltonian of magnetic field and spin-spin interaction $\hat{H}_S$ (Eq. (7)), we have

$$I_S = -\frac{2ie}{\hbar} \sum_{m > m', \sigma} J_{m,m'} S_m S_{m'} [n_m - f_K(\varepsilon_k)] \Gamma_{ML,m}. \quad (37)$$

It means that there is a spontaneous current due to the transient process of spin-spin interactions with the fast damping defined by the coefficient $\Gamma_{ML,m}$. The transient process of spontaneous spin-spin interaction current can occur in the molecular structure both in the presence and absence of any external field. The charge transferred during the time of an electromagnetic pulse with the finite duration is given by $Q = \int_{-\infty}^{\infty} I(t) dt$. In the next section, we shall provide the computation of the electric current with $\langle \hat{c}_k \hat{Q}_{\alpha}^a \hat{c}_m \rangle$ and $\langle \hat{c}_k^+ \hat{Q}_{\alpha}^a \hat{c}_m \rangle$.

V. DIFFERENTIAL EQUATIONS FOR NONEQUILIBRIUM CHARGE TRANSFER

In the form of Markovian approximation for the relaxation induced by the molecule-metal leads coupling for the dynamics of the electron system of the molecular junction, we have derived a closed set of equations for the expectation values of binary operator of $\langle \hat{n}_m \rangle = n_m$ and $\langle \hat{b}_M \rangle = p_M$, which are variables of the annihilation and creation operators for electrons in molecular states $|1\rangle$ and $|2\rangle$. Straightforward operator algebra manipulations yield $n_m$ and $p_M$ in the rotating wave approximations. The expression for nanojunction in the Hartree-Fock approximation $n_1 n_2 + \langle p_M \rangle \langle p_M^+ \rangle = \frac{1}{2} (n_1 + n_2)$, is correct only when the length of the Bloch vector is conserved. However, due to the charge transfer between the molecular orbitals and metals, this value is not conserved. Thus, the so-called relevant density matrix of molecule $\rho_M$ is used as a total density matrix $\rho$, which contains the information of the expectation values of operators $\hat{n}_m$ and $\hat{p}_M$. If chosen appropriately, the relevant density matrix contains the essential part of the molecular dynamics, but we employ the following
properties \[53, 56\]: \( T r(\hat{n}_1\hat{n}_2\rho_M) = |p_M|^2 + n_1n_2 \). Due to the assumption mentioned above, the scattering rate of populations depends on the polarization \( \hat{p}_M \) which is similar to the case of semiconductor Bloch equations \[56\]. It is assumed that the polarization is small, so that in the final scattering terms they keep only the terms linear to the polarization \[56\]. The advantage of our approach to the molecular junction is that it could also be used when the dissipative system (metals) is not in equilibrium and the many-body effects are significant.

In this case, the total density matrix is \( \rho = \rho_M \prod_{k \in L,R} \rho_k \). By taking into account the formal mathematical methods, the derivation of the differential equations for the expectation values from the Heisenberg equations are reported\[41, 56\]. Employing Eqs. (30), (31) and (34) as well as (D1), (D2) and (D6) in Appendix D for the polarization, we finally obtain

\[
\frac{dp_M}{dt} = -i[\omega_0 + \sum_{K=L,R} \Delta_{MK} - \omega(t)]p_M - \frac{i}{2} \Omega_R \left( \sum_{m \in M} n_m - 1 \right) - p_M \Gamma_{PM}
\]

(38)

where \( \omega(t) = \omega_0 + \mu(t - t_0) \), \( \mu \) is a chirp rate,

\[
\Gamma_{PM} = \sum_{K=L,R} \left\{ \frac{1}{2} (\Gamma_{MK,1} + \Gamma_{MK,2}) + \Gamma_{NK}[\omega(t)] \right\}
\]

(39)

and

\[
\Delta_{MK} = \frac{1}{\hbar} \sum_{k \in K} \left| \frac{V_{k1}^{(MK)}}{\varepsilon_k - \varepsilon_1} - \frac{V_{k2}^{(MK)}}{\varepsilon_k - \varepsilon_2} \right|^2.
\]

(40)

The \( \Omega_R \) is the generalized Rabi frequency\[57\], consisting of two parts.

\[
\Omega_R = g\mu_B \hbar^{-1} B(t) \sum_{m, m' \in M} S_m S_{m'} - 2\hbar^{-1} \sum_{m > m', \sigma \sigma'} J_{m, m'} S_m S_{m'}.
\]

(41)

The first part is the Larmor frequency due to nonstationary magnetic fields and the second part is the spin-spin interaction. The equation for the electron number has the form:

\[
\frac{dn_m}{dt} = \Omega_R \text{Im} p_M + \sum_{K=L,R} \left( f_{MK}(\hbar \omega_0/2) - n_m \right) \Gamma_{MK,m} + 2 \sum_{m \neq m' \in M} \left( n_m - f_K(\varepsilon_k) \right) (n_{Q_m} + n_{Q_m'}) \Gamma_{VK,m} - \sum_{K=L,R} \{ \Gamma_{NK}(\omega_0) [\|p_M\|^2 + \prod_{m \in M} n_m] - \Gamma_{NK}(\omega_0) [1 - \prod_{m \in M} n_m] \}.
\]

(42)
Here we introduce the next basic dynamical variables for the phonon number which is
\[ n_{ph} \equiv \langle \hat{a}_\alpha^+ \hat{a}_\alpha \rangle, \]
and the phonon-assisted density matrices of electron-phonon interaction are
\[ n_{Qm} \equiv \langle \hat{c}_k \hat{Q}_a^\dagger \hat{c}_m \rangle, \quad n_{Pm} \equiv \langle \hat{c}_k \hat{P}_a^\dagger \hat{c}_m \rangle, \quad Q_{\alpha} \equiv \langle \hat{Q}_a^\dagger \rangle, \quad P_{\alpha} \equiv \langle \hat{P}_a^\dagger \rangle \] where \( \hat{P}_{\alpha} = i(\hat{a}_\alpha - \hat{a}_\alpha) \). Within the Heisenberg picture, we have a set of
differential equations for the phonon occupation number \( n_{ph} \) and the expectation values of
\[ n_{Qm} \] and \[ n_{Pm} \] derived in refs. [58, 59, 60, 61]. Substituting Eqs. (C3, C4 and C7, C10) into
Heisenberg equations Eqs. (10,11) and using Pauli commutators and anticommutators Eqs. (A1, A2) for the phonon-electron interaction terms, we finally obtain
\[ \frac{dn_{Qm}}{dt} = \omega_{\alpha} n_{Pm} \\
+ 2i(1 - n_m)Q_{\alpha} \Gamma_{Q,m} - 2i n_m Q_{\alpha} \Gamma_{Q,m} - \frac{1}{2} \sum_{m \neq m'} (n_m - f_{K}(\varepsilon_k)) \Gamma_{V,K,m} \] (43)
\[ \frac{dn_{Pm}}{dt} = -\omega_{\alpha} n_{Qm} + 2i(1 - n_m)P_{\alpha} \Gamma_{Q,m} \\
- 2i n_m P_{\alpha} \Gamma_{Q,m} - 2n_{ph} + 1)\frac{1}{2} \sum_{m \neq m'} (n_m - f_{K}(\varepsilon_k)) \Gamma_{V,K,m} \] (44)
where \( \omega_k = \varepsilon_k / h, \omega_m = \varepsilon_m / h \), and
\[ \frac{dQ_{\alpha}}{dt} = \omega_{\alpha} P_{\alpha} \] (47)
\[ \frac{dP_{\alpha}}{dt} = -\omega_{\alpha} Q_{\alpha} + \sum_{K=L,R} (n_m - f_{K}(\varepsilon_k)) \Gamma_{M,K,m}. \] (48)
The equation for \( n_{ph} \) is
\[ \frac{dn_{ph}}{dt} = \sum_{m \neq m' \in M} (n_m - f_{K}(\varepsilon_k)) \Gamma_{P,m} + \sum_{m \neq m' \in M} n_{Pm} \Gamma_{QM,m}. \] (49)
Here
\[ \Gamma_{QK,m} = \frac{1}{\hbar} \sum_{k \in K} V^{(V)}_{k,m} f_{K}(\varepsilon_k), \]  
(50)

\[ \Gamma_{QK,m} = \frac{1}{\hbar} \sum_{k \in K} V^{(V)}_{k,m} (1 - f_{K}(\varepsilon_k)), \]  
(51)

\[ \Gamma_{VK,m} = \frac{\pi}{\hbar} \sum_{m \neq m^\prime \in M} \sum_{k \in K} V^{(M)}_{m,k} V^{(V)}_{m,m^\prime} f_{K}(\varepsilon_k) \delta(\varepsilon_k - \varepsilon_m), \]  
(52)

\[ \Gamma_{NK}(\omega(t)) = \frac{2\pi}{\hbar} \sum_{k,k^\prime \in K} |V^{(NK)}_{k,k^\prime}|^2 f_{K}(\varepsilon_k) f_{K}(\hbar \omega - \varepsilon_k) \delta(\hbar \omega - \varepsilon_k). \]  
(53)

From Eq. (55) we have a part of the full formula for the current taking into account the electron-phonon interaction:
\[ I_{ph} = -e \sum_{m \neq m^\prime \in M} (n_{Qm} \Gamma_{QK,m} + n_{QK,m} \Gamma_{QK,m}) \]  
(54)

VI. MAGNETIC CONTROL OF CURRENT AND TRANSFERRED CHARGE WITH CHIRPED PULSES

Now we have generalized theoretical results for the charge transfer at the quasi-stationary strong magnetic field limit, as discussed in the previous section. The well-known procedures are based on the coherent excitation which produces the complete population inversion in an ensemble of degenerate two-level molecules with the Rabi population oscillations by the Gaussian pulse excitation [62]. It has been demonstrated that a molecule or an atom excited by the Gaussian pulses behaves as a semiconductor quantum dot [63, 64, 65, 66]. To solve the main problem of the Gaussian pulse excitation of molecular levels, it requires the information of the resonant magnetic source, the precise control of the pulse area, and the chirp rate \( \mu \) [67]. In order to provide the complete population inversion procedure, known as adiabatic rapid passage (ARP) [62, 67, 68, 69, 70, 71, 72], the entire population needs to transform from ground \( |1> \) to the excited \( |2> \) electronic state. Thus, it is necessary to sweep the pulse frequency through a resonance. The mechanism of ARP can be explained by avoided crossing of dressed (adiabatic) states. In particular, starting from state \( |1> \), the system follows the adiabatic state and eventually ends up in state \( |2> \) [70]. The scheme based on ARP is robust since it is insensitive to the pulse area and the precise location of the resonance. Therefore, we shall focus on the following ARP procedures as a way to
control the magnetic field induced charge transfer in molecular spin nanojunctions. Our formalism presented for the coherent magneto-spin properties of nanojunctions of molecular and quantum dots by the Gaussian pulses excitation [66], is analyzed here.

As a particular example, we shall consider a magnetic-induced charge transfer in molecular nanojunctions. The instantaneous magnetic pulse frequency $\omega(t)$ is given as the linear chirped pulses $\omega(t) = \omega_0 - \mu(t - t_0)$ (where chirped rate $\mu$ is constant) during the pulse excitation [67], and the Gaussian pulse of the magnetic field is used as [62, 67, 73]

$$B(t) \equiv B_0 \exp[-\frac{1}{2} (\delta^2 - i\mu)(t - t_0)^2],$$

where $\delta$ is the inverse duration of the pulse and $B_0$ is the amplitude of pulse. $\delta$ and $\mu$ are used in dimensionless units below. Particularly interesting in this respect are molecules characterized by strong charge-transfer transitions that are reflected in the formation of an excited molecular state with a magnetic dipole. When the magnetic fields operate as a molecular dipole connecting two metal leads along the direction of the charge transfer (approximately perpendicular to the current flow axis), the magnetic pumping into the charge-transfer state creates an internal driving force for charge flow between the two leads. Here we will make a reasonable assumption that a charge-transfer transition within the molecule is expressed in terms of the change in relative coupling strengths of the molecular HOMO and LUMO to their metallic contacts. We thus investigate models in which $\Gamma_{MK,1} < \Gamma_{MK,2}, K \in L, R$. This inequality reflects the fact that the excited molecular state is dominated by atomic orbitals of larger amplitude on one side of the molecule than on the other side, resulting in greater overlap with metal orbitals on that side. In the calculation we used the next constants [29, 41]: $\Gamma_{ML,1} = 0.01$ eV, $\Gamma_{ML,2} = 0.02$ eV and $\Gamma_{VK,m} = 0.02$ eV. The numbers taken above for the $\Gamma_{MK,m}$ parameters where $K = \{L, R\}$ and $m = 1, 2$ are reasonable, and in any case we find that similar results are obtained when they are changed within a reasonable range. Also, the choice $0.01 < \Gamma_{VK,m} < 0.1$ eV reflects an assumed lifetime of $\approx 10$ fs for an excited molecule at the metal surface to relax via the electron-phonon mechanism, which is also a reasonable number. The energy of the pulse can be evaluated as 1-10 eV [55]. This number is the order of magnitude of normal magnetic field intensities used in spectroscopy, and it should be kept in mind that it could result from weaker incident fields due to local field enhancement. Figs. [24] show the influence of $\mu$ or the chirp rate in the time domain on the induced current calculated by Eq. [55].
FIG. 2: Current $I$ (in dimensionless unit) as a function of time $\tau = \omega_0 t$ for the linear chirp rate $\mu/\omega_0^2 = 5 \cdot 10^{-3}$ (A), $10^{-2}$ (B), and $10^{-1}$ (C). The parameters of the calculation are as follows: $\delta = 5 \cdot 10^{-3}$, $h\omega_0 = 3$ eV, $\Gamma_{MR,1}/h\omega_0 = 0.04$, $\Gamma_{MR,2}/h\omega_0 = 0.03$, $\Gamma_{NK}/h\omega_0 = 0.01$, $\Gamma_{QM,m} = 0.01$, $\Gamma_{QM,m} = 0.99$. The picture illustrates how the current depends on the linear chirp rate.

in dimensionless form: $I = I(\tau)/e\Gamma_{ML,1}$ during one magnetic pulse action. These results are displayed as a function of dimensionless time $\tau = \omega_0 t$ with the $\mu$ dependence from the numerical solution of Eqs. (38, 49) for a Gaussian pulse. We see that the pulse chirping can increase the amplitudes of the induced current, which can be explained by signatures of ARP (Fig. 2, Fig. 3).

The pulses of the current obtained by changing the separation of pulse compression has to be Lorentzian. The parameter $\delta$ is the inverse pulse duration of the corresponding transform-limited pulse. The chirped frequency $\omega(t)$ changes to the resonance condition during the time of the pulse. Note that the local field of Eqs. (8) and (9) in the nanojunction also reflects magnon excitation in the leads. The incident pulse shape affected only by the compression uses the possible contribution of the near-field response to both plasmonic and magnon excitations in the leads and to excitons in the molecule. The excitation of electric current by the magnetic fields in the spin nanojunction also reflects phonon-electron interaction in the molecule and the leads. The incident pulse shape affected only by the pulse compression excites the phonon-electron interaction toward the broadening of the peak of the current.
FIG. 3: Current $I$ (in dimensionless unit) as a function of time $\tau = \omega_0 t$ for the linear chirp rate
$\mu/\omega_0^2 = 10^{-1}$ (A), $5 \cdot 10^{-2}$ (B) and $10^{-2}$ (C), where $\delta = 10^{-2}$. Other parameters are identical to those of Fig.2. The picture illustrates how signatures of ARP increase the amplitude of the induced current.

response [74, 75]. Such effects are presented in Figs. 2-4. The observable of interest is the magnetic field induced electronic current. Changing bias under magnetic fields with a fixed frequency can make the polar molecule into and out of the resonance by excitation, leading to highly nonlinear current voltage dependence including the possibility for negative differential resistance.

Figs. 5 and 6 show the calculation results of the transferred charge $Q$:

$$Q = \int_{-\infty}^{\infty} I(\tau) d\tau$$

(56)
as a function of the chirp rate $\mu$ in the frequency domain and $\delta$. The calculated dependencies $Q(\mu)$ of Fig.5 and $Q(\delta)$ of Fig.6 are confined to the values of arguments $\mu$ and $\delta$ corresponding to $d_\mu B_0/\hbar \omega_0 \leq 0.3$ ($d_\mu = g \mu_B/2$ is the molecular magnetic dipole moment, Eq.(54)). Since the theory uses the rotating wave approximation, the amplitude of magnetic field has to be limited. One can see that $Q$ grows rapidly for small $\mu$ and $\delta$. Fig.5 shows that the growth of $Q$ is slow for moderate $\delta = 10^{-2}$ and then $Q$ tends to become a constant value for large
FIG. 4: The current $I$ (in dimensionless unit) transferred after the completion of the pulse action as a function of the chirp rate $\mu$ in the frequency domain, $\tau = \omega_0 t$. Here $d_{\mu}B_0/\hbar \omega_0 = 0.2$, $\delta = 10^{-1}$, $\mu/\omega_0^2 = 10^{-2}$ (A), $5 \cdot 10^{-2}$ (B) and $1.5 \cdot 10^{-1}$ (C) for the transform-limited pulse. In the course of chirping, the pulse energy is conserved so that $\int_{-\infty}^{\infty} B^2(t) dt = B_0^2$ is constant. Other parameters are identical to those of Fig.2. The picture illustrates the manifestation of ARP, i.e. how the amplitude of the current increases with increasing chirp rate $\mu$.

FIG. 5: Charge $Q$ (in dimensionless unit) transferred after the completion of the pulse action as a function of the chirp rate $\mu$ for the transform-limited pulse. Here, $d_{\mu}B_0/\hbar \omega_0 = 0.2$, $\delta = 10^{-3}$ (A), $\delta = 5 \cdot 10^{-3}$ (B), and $\delta = 10^{-2}$ (C). Other parameters are identical to those of Fig.2. The picture illustrates the manifestation of ARP, i.e., how the quantity of the charge increases with increasing chirp rate $\mu$. 
FIG. 6: Charge $Q$ (in dimensionless unit) transferred after the completion of the pulse action as a function of $\delta$ in the presence of energy transfer. Chirp rate is $\mu = 5 \cdot 10^{-3}$ (A), $\mu = 10^{-2}$ (B), and $\mu = 5 \cdot 10^{-2}$ (A). Other parameters are identical to those of Fig.4.

$\delta = 10^{-3}$. The large pulse energy is larger than the value of $Q$ at which the growth of $\delta$ slows down as presented in Figs. 5 and 6 which illustrate the influence of the energy transfer that diminishes the corresponding values of $Q$ (see also Figs. 2 and 3). Figs. 5 and 6 show the resulting behavior of the charge current induced by magnetic fields from Eq.(55), based on the full self-consistent calculation described in Sec. II. The parameters used in this calculation are $T = 300$ K. As expected, a steady state current flows through the spin nanojunction in the presence of magnetic pumping. A peak of the current occurs at the frequency of the charge-transfer transition, i.e., the HOMO-LUMO energy gap in our model. The fact that magnetic current can occur in a molecular spin nanojunction with the postulated characteristics is a direct consequence of the fact that the charge-transfer properties of the molecules lead to an internal driving force that would result in magnetic voltage in the corresponding open circuit. Another point of concern is the thermal stability of spin nanojunction under the proposed thermal heating. On the other hand, the current calculated with these parameters (Figs. 2-4) is of order 1 nA, implying that the magnetic intensity which is lower by an order of magnitude can still lead to observable currents. We conclude that the magnetic current in a molecular spin nanojunction is a realistic possibility. The values of $Q$ shown in Fig. 6 can be rationalized by the theoretical consideration below.
It illustrates the influence of $\delta$ of magnetic pulse, the carrier pulse frequency $\omega$, and the corrected frequency of the molecular transition $\omega_0$ on the transferred charge $Q$. As shown in Fig. 6, there is an optimal parameter for magnetic pulses to provide the maximum of $Q$. This picture shows us the solution to the optimal control of the parameters of the pulse in order to obtain the maximum charge transfer. To end this section we note that the current corresponding to the expectation value of $Q$ is $0.7 \cdot 10^{-19} \text{ C}$ per pulse (corresponding to curve C in Fig. 6) and the estimated pulse repetition frequency of 82 MHz results in a small but measurable value of about $10 \times 10^{-12} \text{ ampere}$. When the energy transfer between the molecule and electron-phonon excitations in the molecules and leads is present for the linear chirp, this control model can complicate the Landau-Zerner transition to a decaying level, which were solved in Refs. [41] and [76]. The relaxation parameters in the derived closed set of the equations of motion do not depend on the exciting magnetic field and the phonon numbers. The present theory could be supplied by an additional equation described by thermal bath, as was shown in Ref. [51], in the case when the Rabi frequency $\Omega_R$ is much smaller than the bath correlation frequency $\omega_c$. If molecular states $\varepsilon_m$ are far from the Fermi levels of both leads, $\omega_c$ is determined by the frequency interval for the system-bath interaction matrix elements $V_{km}^{(MK)}$ and $V_{kk'}^{(NK)}$ and the density of states of metal leads. The approximation of constant relaxation parameters, which do not depend on exciting magnetic radiation, is consistent with the rotating wave approximation used in our theory. The situation is different if we assume that the orbital energy molecular level is pinned to the Fermi energy of a lead. This may lead to highly nonlinear current voltage dependence [29]. In this case, $\omega_c$ is determined also by the frequency interval at which $f_K(\varepsilon)$ is essentially changed by $\sim k_B T / \hbar$. $\Omega_R$ can be of the same order of magnitude with $\omega_c$ in the rotating wave approximation, and the dependence of the relaxation parameters on exciting magnetic field [55] has to be included in the theory.

VII. CONCLUSION

We have investigated a model process driven by magnetic fields in a molecular system connecting metal leads. We considered the general theoretical aspects of the interaction of a molecular spin nanojunction with the magnetic field within a single-electron model. A simple conduction model for the HOMO and LUMO of a molecule is given in the presence of the
magnetic field when the electronic distribution in the molecule is far from equilibrium under bias voltage. This nonequilibrium state is associated with the electron flux between the source and leads, energy flux between the nonequilibrium molecular electronic distribution, and the local electronic distribution in the metals leads. This is a nonradiative dissipation mechanism that couples electronic excitations in the molecule to excitons in the metal. We have investigated two aspects of the interrelationships between electron fluxes. First, we have calculated the dependence of the current pulse shape of the molecule on the parameters of Gaussian pulse. Second, we have studied the condition under which current may be induced without bias voltage by the external magnetic field to adjust a nonequilibrium steady state. Due to the competing relaxation processes, the magnetic field induced current suggests that the observation is feasible. The control of electron transfer by magnetic fields in a metal-molecule-metal spin nanojunction is not a simple task. The theory can be useful for the development of the treatment of negative differential resistance and giant magnetoresistance in molecular spin nanojunctions. The present results suggest that the experiments for an observation of ARP are indeed feasible. We derived the explicit solution of general case for the current Eq. (35). It is shown that the system excited by magnetic field has an additional combination frequency. The differential equations Eqs. (44) and (46) contain new additional combinational frequencies depending on the concentrations of molecular electrons and fermi functions. The additional combination part of the current is the effective tool to measure the concentration of molecular electrons and it can be extended to measuring the concentration of the charge carriers for another nanodevice.

As was mentioned in Sec. II, future generations of the spintronic molecular systems would employ the coherent magnetic manipulations. We considered such coherent control processes for the adjustment of $Q$ by pulse with independent parameters of $\mu$ and $\delta$. Both the transfer driven current and charge that give rise to the net current in the biased spin nanojunction and the energy transfer between the molecule and electron-phonon excitations in the molecules and leads can grow with growing $\mu$ and $\delta$ regardless of the loss of energy. It should be emphasized that all processes considered in this work may play important roles in spin nanojunction in response to the incident magnetic fields. First, direct electron-phonon excitations of the molecular system and the metal leads may affect the response to an adsorbed molecule that is beyond the local field enhancement associated with the local excitation. Second, experimental realization of strong local excitations in nanojunctions requires
careful consideration of phonon dissipation and conduction [78]. Phonon-electron interaction and phonon excitation may be kept under control by the junction using a sequence of well separated magnetic pulses, as noted in the proposed experiment.

**Acknowledgement** This work was supported by KOSEF (WCU: R32-2008-000-10180-0, EPB Center: R11-2008-052-01000), BK21(KRF), and GRL (KICOS). We thank B. Fainberg for discussion.

**APPENDIX A: HEISENBERG EQUATION FOR THE ELECTRON - MOLECULE INTERACTION**

We use the following Pauli commutators:

\[
\begin{align*}
[\hat{c}_i, \hat{c}^+_j] &\equiv \hat{c}_i\hat{c}^+_j + \hat{c}^+_j\hat{c}_i = \delta_{ij}, \\
[\hat{c}_i, \hat{c}_j] &\equiv [\hat{c}^+_i, \hat{c}^+_j] \equiv \hat{c}_i\hat{c}_j + \hat{c}_j\hat{c}_i = 0.
\end{align*}
\]

(A1) (A2)

where \( \hat{c}_i \) and \( \hat{c}^+_j \) are Fermi operators, \( \delta_{ij} \) is the Kroenecker delta, and \( \hat{c}^+_i\hat{c}_i = \hat{n}_i, \hat{c}_i\hat{c}^+_i = 1 - \hat{n}_i. \)

For the unperturbed Hamiltonian \( H_0 \) in Eq.(2), we have

\[
[\hat{H}_0, \hat{c}_m] = - \sum_{m' \in M} \varepsilon_{m'} (\hat{c}^+_m\hat{c}_m + \hat{c}_m\hat{c}^+_m)\hat{c}_{m'} = -\varepsilon_m\hat{c}_m.
\]

(A3)

The corresponding terms for \( c_k(c^+_k) \) in the Heisenberg equations is

\[
[\hat{H}_0, \hat{c}_k] = - \sum_{k' \in K} \varepsilon_{k'} (\hat{c}^+_k\hat{c}_{k'} + \hat{c}_{k'}\hat{c}^+_k)\hat{c}_{k'} = -\varepsilon_k\hat{c}_k.
\]

(A4)

In Eq.(11) the interaction term of electrons in the molecule \( \hat{V}_M \) has

\[
[\hat{V}_M, \hat{c}_m] = \sum_{K=L,R} \sum_{m',m \in M;k \in K} \{-V^{(MK)}_{km'} (\hat{c}^+_k\hat{c}_m + \hat{c}_m\hat{c}^+_m)\hat{c}_{m'}
- V^{(MK)}_{m'k} (\hat{c}^+_m\hat{c}_m + \hat{c}_m\hat{c}^+_m)\hat{c}_k\} = - \sum_{K=L,R} \sum_{k \in K} V^{(MK)}_{mk} \hat{c}_k,
\]

(A5)

and the interaction term of electrons in the leads has

\[
[\hat{V}_M, \hat{c}_k] = \sum_{K=L,R} \sum_{m',m \in M;k',k \in K} \{-V^{(MK)}_{k'm'} (\hat{c}^+_k\hat{c}_m + \hat{c}_m\hat{c}^+_m)\hat{c}_{m'}
- V^{(MK)}_{m'k'} (\hat{c}^+_m\hat{c}_m + \hat{c}_m\hat{c}^+_m)\hat{c}_{k'}\} = - \sum_{m' \in M} V^{(MK)}_{km'} \hat{c}_{m'}.
\]

(A6)
To simplify the representation of Hamiltonian Eq. (14) of the energy transfer, we take into account \( m \in M \), where \( M = \{1, 2\} \) (where 1, 2 denotes the HOMOs and LUMO). Then, the Poisson brackets of the electrons in the molecule have the form:

\[
[V_N, \hat{c}_m] = \sum_{K=L,R} \sum_{k \neq k' \in K} \{ V_{kk'}^{(NK)} (\hat{c}^+_k \hat{c}_k \hat{c}_m \hat{c}_c + \hat{c}^+_c \hat{c}_c \hat{c}_m \hat{c}_k) + V_{kk'}^{(NK)} (\hat{c}^+_1 \hat{c}_2 \hat{c}_k \hat{c}_m - \hat{c}_m \hat{c}^+_1 \hat{c}_2 \hat{c}^+_k \hat{c}_k) \}
\]

\[
= - \sum_{K=L,R} \sum_{k \neq k' \in K} \{ V_{kk'}^{(NK)} \hat{c}^+_k \hat{c}_k (\hat{c}^+_1 \hat{c}_2 \hat{m} + \hat{c}_m \hat{c}^+_2 \hat{c}_1) + V_{kk'}^{(NK)} \hat{c}^+_k \hat{c}_k (\hat{c}^+_1 \hat{c}_2 \hat{c}_m + \hat{c}_m \hat{c}^+_2 \hat{c}_1) \delta_{1m} (\hat{c}^+_1 \hat{c}_1 + \hat{c}_1 \hat{c}^+_1) \hat{c}_2 \hat{c}_k \hat{c}_k \}
\]

\[
= - \sum_{K=L,R} \sum_{k \neq k' \in K} \{ V_{kk'}^{(NK)} \hat{c}^+_k \hat{c}_k \hat{c}_1 \delta_{2m} + V_{kk'}^{(NK)} \hat{c}^+_k \hat{c}_k \hat{c}_1 \delta_{2m} + \}
\]

The Poisson brackets for the lead electrons have the form:

\[
[V_N, \hat{c}_k] = \sum_{K=L,R} \sum_{k \neq k' \neq k'' \in K} \{ V_{kk'}^{(NK)} (\hat{c}^+_k \hat{c}^+_k \hat{c}_k \hat{c}_k + \hat{c}^+_k \hat{c}^+_k \hat{c}_k \hat{c}_k), \hat{c}_k \}
\]

\[
= \sum_{K=L,R} \sum_{k \neq k' \neq k'' \in K} \{ V_{kk'}^{(NK)} (\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) + V_{kk'}^{(NK)} (\hat{c}^+_1 \hat{c}^+_2 \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_1 \hat{c}^+_2 \hat{c}^+_k \hat{c}_k) \}
\]

\[
= \sum_{K=L,R} \sum_{k \neq k' \neq k'' \in K} \{ V_{kk'}^{(NK)} (\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) + V_{kk'}^{(NK)} (\hat{c}^+_1 \hat{c}^+_2 \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_1 \hat{c}^+_2 \hat{c}^+_k \hat{c}_k) \}
\]

\[
= \sum_{K=L,R} \sum_{k \neq k' \neq k'' \in K} \{ V_{kk'}^{(NK)} (\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k + \hat{c}^+_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) \}
\]

\[
= - \sum_{K=L,R} \sum_{k \neq k' \neq k'' \in K} V_{kk'}^{(NK)} (\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k + \hat{c}^+_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) = - \sum_{k \neq k' \neq k'' \in K} V_{kk'}^{(NK)} (\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k + \hat{c}^+_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) \}
\]

To obtain the formulas presented above, we used the following rules of the triadic multiplication for operators. If \( k \neq k' \), then \((\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) = - (\hat{c}^+_k \hat{c}_k \hat{c}_k) = \delta_{kk'} \hat{c}^+_k \hat{c}_k \).

If \( k = k' \), then \((\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) = - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k = 0 \), since \( k'' \neq k' \). Therefore, we have \((\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) = - \delta_{kk'} \hat{c}^+_k \hat{c}_k \).

If \( k \neq k' \), then \((\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) = - \delta_{kk' \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k} \).

If \( k = k' \), then \((\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) = - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k = 0 \). Therefore, we have \((\hat{c}^+_k \hat{c}^+_k \hat{c}^+_k \hat{c}_k - \hat{c}_k \hat{c}^+_k \hat{c}_k \hat{c}^+_k \hat{c}_k) = - \delta_{kk'} \hat{c}^+_k \hat{c}_k \).
APPENDIX B: HEISENBERG EQUATION FOR THE ELECTRON - MAGNETIC FIELD INTERACTION

In the Heisenberg equation with the magnetic fields (11), the term of $\hat{H}_B$ in Eq.(8) for the interaction of the electron in the molecular system $c_m$ has the form:

$$\hat{H}_B = -\mathbf{H}_B(r,t)(\hat{c}_2^+ \hat{c}_1 + \hat{c}_1^+ \hat{c}_2)$$

$$= -\frac{1}{2}(g\mu_B \cdot \mathbf{e})\{\hat{c}_2^+ \hat{c}_1 \mathcal{B}(t) \exp[-i\omega t + i\varphi(t)]$$

$$+ \hat{c}_1^+ \hat{c}_2 \mathcal{B}^*(t) \exp[i\omega t - i\varphi(t)]\}$$

(B1)

where $\mathbf{e}$ is the unit vector. Substituting Eq.(B1) in the Poisson brackets of Eq.(11), we have

$$[\hat{H}_B, \hat{c}_m] = -\frac{1}{2}(g\mu_B \cdot \mathbf{e})[\hat{c}_2^+ \hat{c}_1 \mathcal{B}(t) \exp[-i\omega t + i\varphi(t)]$$

$$+ \hat{c}_1^+ \hat{c}_2 \mathcal{B}^*(t) \exp[i\omega t - i\varphi(t)], \hat{c}_m]\$$

$$= -\frac{1}{2}(g\mu_B \cdot \mathbf{e})\{(\hat{c}_2^+ \hat{c}_1 \hat{c}_m - \hat{c}_m \hat{c}_2^+ \hat{c}_1)\mathcal{B}(t) \exp[-i\omega t + i\varphi(t)]$$

$$+ (\hat{c}_1^+ \hat{c}_2 \hat{c}_m - \hat{c}_m \hat{c}_1^+ \hat{c}_2)\mathcal{B}^*(t) \exp[i\omega t - i\varphi(t)]\}.$$  (B2)

Taking into account that $m \in M, M = \{1, 2\}$ for Eq.(B2), we have:

$$[\hat{H}_B, \hat{c}_1] = \frac{1}{2}(g\mu_B \cdot \mathbf{e})\mathcal{B}^*(t) \exp[i\omega t - i\varphi(t)]\hat{c}_2$$

and

$$[\hat{H}_B, \hat{c}_2] = \frac{1}{2}(g\mu_B \cdot \mathbf{e})\mathcal{B}(t) \exp[-i\omega t + i\varphi(t)]\hat{c}_1.$$  

Similar to this, the Poisson brackets of Eq.(11) for the magnetic field and the lead electrons yield:

$$[\hat{H}_B, \hat{c}_k] = -\mathbf{H}_B(r,t)[\hat{c}_2^+ \hat{c}_1 + \hat{c}_1^+ \hat{c}_2, \hat{c}_k]$$

$$= -\mathbf{H}_B(r,t)\{(\hat{c}_2^+ \hat{c}_1 \hat{c}_k - \hat{c}_k \hat{c}_2^+ \hat{c}_1) + (\hat{c}_1^+ \hat{c}_2 \hat{c}_k - \hat{c}_k \hat{c}_1^+ \hat{c}_2)\}$$

$$= -\mathbf{H}_B(r,t)\{(\hat{c}_2^+ \hat{c}_1 - \hat{c}_2^+ \hat{c}_1)\hat{c}_k + (\hat{c}_1^+ \hat{c}_2 - \hat{c}_1^+ \hat{c}_2)\hat{c}_k\} = 0.$$  

27
APPENDIX C: HEISENBERG EQUATION FOR THE ELECTRON - PHONON INTERACTIONS IN THE MOLECULE

In the Heisenberg equation (11), the term of $\hat{V}_V$ in the interaction of molecular phonons $\hat{Q}_\alpha$ and electrons $c_k$ has the form:

$$\frac{dc_m}{dt} = \frac{i}{\hbar} \left[ \hat{V}_V, c_m \right] = -\frac{i}{\hbar} \sum_{m \neq m' \in M} (V_{mm'}(VK)\hat{Q}_\alpha)\hat{c}_{m'},$$ \hspace{1cm} (C1)

$$\frac{d\hat{c}_m}{dt} = \frac{i}{\hbar} \left[ \hat{V}_V, \hat{c}_m \right] = -\frac{i}{\hbar} \sum_{m \neq m' \in M} (V_{mm'}(VK)\hat{Q}_\alpha)\hat{c}_{m'}^+.$$ \hspace{1cm} (C2)

Following the phonon commutation rules $[a_\alpha, a_\alpha^+] = 1$ for the Poisson brackets of the interaction of molecular phonons and electrons, we have

$$\left[ \hat{H}_0, \hat{c}_k \hat{Q}_\alpha \hat{c}_m^+ \right] = -\sum_\alpha i\omega_\alpha \hat{c}_k \hat{P}_\alpha \hat{c}_m^+,$$ \hspace{1cm} (C3)

$$\left[ \hat{H}_0, \hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m \right] = -\sum_\alpha i\omega_\alpha \hat{c}_k^+ \hat{P}_\alpha \hat{c}_m + \sum_{m \in M, k \in K} (\varepsilon_k - \varepsilon_m) \hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m$$

$$+ \sum_{m \in M, k \in K} 2(\varepsilon_m n_m - \varepsilon_k f_K(\varepsilon_k)) \hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m,$$ \hspace{1cm} (C4)

$$\left[ \hat{H}_0, \hat{c}_k \hat{P}_\alpha \hat{c}_m^+ \right] = \sum_\alpha i\omega_\alpha \hat{c}_k \hat{Q}_\alpha \hat{c}_m^+,$$ \hspace{1cm} (C5)

$$\left[ \hat{H}_0, \hat{c}_k^+ \hat{P}_\alpha \hat{c}_m \right] = \sum_\alpha i\omega_\alpha \hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m + \sum_{m \in M, k \in K} (\varepsilon_k - \varepsilon_m) \hat{c}_k^+ \hat{P}_\alpha \hat{c}_m$$

$$+ \sum_{m \in M, k \in K} 2(\varepsilon_m n_m - \varepsilon_k f_K(\varepsilon_k)) \hat{c}_k^+ \hat{P}_\alpha \hat{c}_m,$$ \hspace{1cm} (C6)

$$\left[ \hat{V}_M, \hat{c}_k \hat{Q}_\alpha \hat{c}_m^+ \right] = 2 \sum_{K=L,R} \sum_{m \in M, k \in K} V_{km}^{(MK)}((1 - n_m)f_K(\varepsilon_k)$$

$$- (1 - f_K(\varepsilon_k))n_m)\hat{Q}_\alpha,$$ \hspace{1cm} (C7)

$$\left[ \hat{V}_M, \hat{c}_k^+ \hat{P}_\alpha \hat{c}_m \right] = 2 \sum_{K=L,R} \sum_{m \in M, k \in K} V_{km}^{(MK)}((1 - n_m)f_K(\varepsilon_k)$$

$$- (1 - f_K(\varepsilon_k))n_m)\hat{P}_\alpha,$$ \hspace{1cm} (C8)
\[ [\hat{V}_M, \hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m] = [\hat{V}_M, \hat{c}_k^+ \hat{P}_\alpha \hat{c}_m] = 0 \]  \hspace{1cm} (C9)

\[ [\hat{V}_V, \hat{c}_k \hat{Q}_\alpha^+ \hat{c}_m] = \sum_{m \neq m' \in M} V_{mm'}^{(VK)} (1 - 2n_m) \hat{c}_k \hat{c}_m^2, \]  \hspace{1cm} (C10)

\[ [\hat{V}_V, \hat{c}_k^+ \hat{Q}_\alpha \hat{c}_m] = \sum_{m \neq m' \in M} V_{mm'}^{(VK)} (2n_m + 1) \hat{c}_k^+ \hat{c}_m Q^2_\alpha, \]  \hspace{1cm} (C11)

\[ [\hat{V}_V, \hat{c}_k \hat{Q}_\alpha^+ \hat{c}_m] = \sum_{m \neq m' \in M} V_{mm'}^{(VK)} \hat{c}_m^+ \hat{c}_m, \]  \hspace{1cm} (C12)

**APPENDIX D: CALCULATION OF \( \langle \hat{c}_k^+ \hat{c}_m \rangle \) IN THE PRESENCE OF A MAGNETIC FIELD**

In this section we calculate the expression for the expectation value \( \langle \hat{c}_k^+ \hat{c}_m \rangle \) by taking into account the magnetic field, namely using Eqs. (12), (13), (33) and (32). For \( m = 1 \), we obtain

\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_1 \rangle = \frac{i}{\hbar} (\varepsilon_k - \varepsilon_1) \langle \hat{c}_k^+ \hat{c}_1 \rangle + \frac{i}{\hbar} \sum_{m' = 1, 2} V_{m'k}^{(MK)} \langle \hat{c}_{m'}^+ \hat{c}_1 \rangle - \frac{i}{\hbar} \sum_{K = L, R} \sum_{k' \in K} V_{1k'}^{(MK)} \langle \hat{c}_k^+ \hat{c}_{k'} \rangle \\
+ \frac{i}{\hbar} \sum_{k' \neq k \in K} V_{k'k}^{(NK)} \langle \hat{c}_{k'}^+ \hat{c}_1 \hat{c}_2 \hat{c}_1 \rangle + \frac{i}{2\hbar} (g\mu_B \cdot \mathbf{e}) B^* (t) \exp[\imath \omega t - \imath \phi (t)] \langle \hat{c}_k^+ \hat{c}_2 \rangle \\
- \frac{i}{\hbar} \sum_{K = L, R} \sum_{k'' \neq k' \in K} \langle V_{k''k'}^{(NK)} \hat{c}_{k''}^+ \hat{c}_2 \hat{c}_k^+ \hat{c}_{k'} \rangle \hspace{1cm} (D1)
\]

Since the term \( \langle \hat{c}_{m'}^+ \hat{c}_m \rangle \mid_{m \neq m'} \) is the non-resonant case for multiplication of \( \varepsilon_k - \varepsilon_2 \) and \( \varepsilon_k - \varepsilon_1 \), we must put \( \langle \hat{c}_{m'}^+ \hat{c}_m \rangle = \langle \hat{c}_{m'}^+ \hat{c}_m \rangle \delta_{mm'} \) in the second term on the right-hand side of Eqs. (D1) and (D2). For \( m = 2 \),
by substituting Eq. (D4) for Eq. (D3), we have

\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_2 \rangle = \frac{i}{\hbar} (\varepsilon_k - \varepsilon_2) \langle \hat{c}_k^+ \hat{c}_2 \rangle + \frac{i}{\hbar} \sum_{m' = 1,2} V_{m'k}^{(MK)} \langle \hat{c}_{m'}^+ \hat{c}_2 \rangle
\]

\[
- \frac{i}{\hbar} \sum_{K = L, R, k' \in K} V_{2k'}^{(MK)} \langle \hat{c}_k^+ \hat{c}_{k'} \rangle
\]

\[
+ \frac{i}{\hbar} \sum_{k' \in K} V_{k'k}^{(NK)} \langle \hat{c}_k^+ \hat{c}_{k'} \hat{c}_1 \hat{c}_2 \rangle + \frac{i}{2\hbar} (g\mu_B \cdot e) B(t) \exp[-i\omega t + i\varphi(t)] \langle \hat{c}_k^+ \hat{c}_2 \rangle - \frac{i}{\hbar} \sum_{K = L, R, k' \in K} \sum_{k'' \neq k'} V_{k''k}^{(NK)} \langle \hat{c}_k^+ \hat{c}_{k''} \hat{c}_{k'} \hat{c}_{k''} \rangle
\]

(D2)

In addition, using Eq. (20) and disregarding terms of \( \sim V^{(NK)} \) as a first step, we obtain

\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_m \rangle = \frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \langle \hat{c}_k^+ \hat{c}_m \rangle + \frac{i}{\hbar} V_{mk}^{(MK)} n_m - \frac{i}{\hbar} V_{mk}^{(MK)} f_K(\varepsilon_k)
\]

\[
+ \frac{i}{2\hbar} (g\mu_B \cdot e) B^*(t) \exp[i\omega t - i\varphi(t)] \langle \hat{c}_k^+ \hat{c}_{m'} \rangle .
\]

(D3)

In order to derive the solution of Eqs. (D1)(D2) we shall use the slowly varying amplitude method. Let us define

\[
\langle \hat{c}_k^+ \hat{c}_m \rangle = \langle \hat{c}_k^+ \hat{c}_m \rangle_0 \exp[i\omega t - i\varphi(t)],
\]

(D4)

by substituting Eq. (D4) for Eq. (D3), we have

\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_m \rangle = \frac{i}{\hbar} (\varepsilon_k - \varepsilon_1) \langle \hat{c}_k^+ \hat{c}_m \rangle_0 \exp[i\omega t - i\varphi(t)] + \frac{i}{\hbar} V_{mk}^{(MK)} n_m - \frac{i}{\hbar} V_{mk}^{(MK)} f_K(\varepsilon_k) + \frac{i}{2\hbar} (g\mu_B \cdot e) B^*(t) \exp[i\omega t - i\varphi(t)] \langle \hat{c}_k^+ \hat{c}_{m'} \rangle .
\]

(D5)

Conserving only the resonance terms in Eq. (D5), we have

\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_m \rangle_0 = i[(\varepsilon_k - \varepsilon_m) / \hbar - \omega(t)] \langle \hat{c}_k^+ \hat{c}_m \rangle_0 + \frac{i}{2\hbar} (g\mu_B \cdot e) B^*(t) \langle \hat{c}_k^+ \hat{c}_{m'} \rangle .
\]

(D6)

Integrating the last equation, we obtain

\[
\langle \hat{c}_k^+ \hat{c}_m \rangle_0 = \frac{i}{2\hbar} (g\mu_B \cdot e) B^*(t) \langle \hat{c}_k^+ \hat{c}_{m'} \rangle \int_0^\infty d\tau \exp[i((\varepsilon_k - \varepsilon_m) / \hbar - \omega(t))\tau].
\]

(D7)
\[
\frac{d}{dt} \langle \hat{c}_k^+ \hat{c}_m \rangle = \frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \langle \hat{c}_k^+ \hat{c}_m \rangle + \frac{i}{\hbar} V_{mk}^{(MK)} n_m - \frac{i}{\hbar} V_{mk}^{(MK)} f_K(\varepsilon_k) + \frac{i}{2\hbar} (g\mu_B \cdot \mathbf{e}) B(t) \langle \hat{c}_k^+ \hat{c}_{m' \neq m} \rangle_0,
\]
and

\[
\langle \hat{c}_k^+ \hat{c}_m \rangle \sim \frac{i}{\hbar} V_{mk}^{(MK)} [n_m(t) - f_K(\varepsilon_k)] \int_0^\infty d\tau \exp\left[\frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \tau\right] - \frac{1}{4\hbar^2} (g\mu_B \cdot \mathbf{e})^2 |B(t)|^2 \langle \hat{c}_k^+ \hat{c}_m \rangle \int_0^\infty d\tau \exp\left[\frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \tau\right] \int_0^\infty d\tau \exp\left[i((\varepsilon_k - \varepsilon_{m' \neq m})/\hbar - \omega(t))\tau\right].
\]

(E8)

or

\[
\langle \hat{c}_k^+ \hat{c}_m \rangle \approx \frac{i}{\hbar} V_{mk}^{(MK)} [n_m(t) - f_K(\varepsilon_k)] \int_0^\infty d\tau \exp\left[\frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \tau\right] \left\{1 - \frac{1}{4\hbar^2} (g\mu_B \cdot \mathbf{e})^2 |B(t)|^2 \int_0^\infty d\tau \exp\left[\frac{i}{\hbar} (\varepsilon_k - \varepsilon_m) \tau\right] \int_0^\infty d\tau \exp\left[i((\varepsilon_k - \varepsilon_{m' \neq m})/\hbar - \omega(t))\tau\right]\right\}
\]

(D10)

The last equation gives "saturation" corrections to the preliminary result Eq.(24) by taking into account the external magnetic fields. The approximation for the magnetic field dependent series could be produced by formal integration of Eq.(D10) with an appropriate treatment related to the magnetic field dependent relaxation parameters, namely

\[
\langle \hat{c}_k^+ \hat{c}_m \rangle \approx (n_m(t) - f_K(\varepsilon_k))(1 - |B(t)|^2 \Gamma_{BK,m}) \Gamma_{MK,m},
\]

(D11)

where

\[
\Gamma_{BK,m} = \frac{\hbar^2 (g\mu_B \cdot \mathbf{e})^2 \mathcal{P}^2}{(\varepsilon_k - \varepsilon_m)^2} \Gamma_{MK,m}.
\]

(D12)

APPENDIX E: SIMPLIFIED EQUATIONS OF CURRENT FOR THE $\hat{V}_M$ INTERACTION

In this section we derive the simplified formula for the current and set the differential equations for $n_1$ and $n_2$ without $\hat{V}_V$, $\hat{V}_N$ and $\hat{H}_B$. Using the formula for the current Eq.(35), we obtain

\[
I = e \{[-f_L(\varepsilon_1) + n_1] \Gamma_{ML,1} + [n_2 - f_L(\varepsilon_2)] \Gamma_{ML,2}\}.
\]

(E1)
For $K \in L, R$, the damping coefficient has the form:

$$\Gamma_{MK,1} = \frac{2\pi}{\hbar} \sum_{k \in K} |V_{1k}^{(MK)}|^2 \delta(\varepsilon_{1k} - \hbar \omega_0 / 2),$$  \hspace{1cm} (E2)$$

$$\Gamma_{MK,2} = \frac{2\pi}{\hbar} \sum_{k \in K} |V_{2k}^{(MK)}|^2 \delta(\varepsilon_{2k} - \hbar \omega_0 / 2).$$  \hspace{1cm} (E3)$$

The ordinary differential equation Eq. (42) has the simplified forms:

$$\frac{dn_1}{dt} = \Omega_R \text{Im} \, p_M + \sum_{K=L,R} [f_{1K}(\hbar \omega_0 / 2) - n_1] \Gamma_{MK,1}$$  \hspace{1cm} (E4)$$

$$\frac{dn_2}{dt} = \Omega_R \text{Im} \, p_M - \sum_{K=L,R} [n_2 - f_{2K}(\hbar \omega_0 / 2)] \Gamma_{MK,2}.$$  \hspace{1cm} (E5)$$

The differential equation for the polarization Eq. (38) has the form:

$$\frac{dp_M}{dt} = -i[\omega_0 + \sum_{K=L,R} \Delta_{MK} - \omega(t)] p_M - \frac{i}{2} \Omega_R (n_1 + n_2 - 1) - \frac{1}{2} \sum_{K=L,R} (\Gamma_{MK,2} + \Gamma_{MK,1}) p_M.$$  \hspace{1cm} (E6)$$

[1] G. Binasch, P. Grünberg, F. Saurenbach, and W. Zinn, Phys. Rev. B 39, 4828 (1989).
[2] M. N. Baibich, J. M. Broto, A. Fert, F. N. Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. 61, 2472 (1988).
[3] S. S. P. Parkin, N. More, and K. P. Roche, Phys. Rev. Lett. 64, 2304 (1990).
[4] Y. Asano, A. Oguri, and S. Maekawa, Phys. Rev. B 48, 6192 (1993).
[5] J. S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, Phys. Rev. Lett. 74, 3273 (1995).
[6] J. S. Moodera, J. Nowak, and R. J. M. van de Veerendonk, Phys. Rev. Lett. 80, 2941 (1998).
[7] H. Mehrez, J. Taylor, H. Guo, J. Wang, and C. Roland, Phys. Rev. Lett. 84, 2682 (2000).
[8] W. Kim and K. Kim, Nature Nanotech. 3, 408 (2008).
[9] G. Gamov, Z. Phys 51, 204 (1928).
[10] MRS Bull. Special issue on molecular junctions, edited by C. R. Kagan and M. A. Ratner. 29, 376 (2004).
[11] Proc. Natl. Acad. Sci. USA. Special issue on molecular electronics, edited by C. Joachim and M.A.Ratner. 102, 8800 (2005).
[12] S. Kohler, J. Lehmann, S. Camalet, and P. Hanggi, Israel J. of Chem. 42, 135 (2002).
[13] S. Kohler, S. Camalet, M. Strass, J. Lehmann, G.-L. Ingold, and P. Hanggi, Chem. Phys. 296, 243 (2004).
[14] W. Y. Kim, S. K. Kwon, and K. S. Kim, Phys. Rev. B 76, 033425 (2007).
[15] M. Diefenbach and K. S. Kim, Angew. Chem. Int. Ed. 46, 7640 (2007).
[16] D. Dulic, S. van der Molen, T. Kudernac, H. Jonkman, J. de Jong, T. Bowden, J. van Esch, B. Feringa, and B. van Wees, Phys. Rev. Lett. 91, 207402 (2003).
[17] N. Katsonis, T. Kudernac, M. Wallko, and et al., Adv. Materials 18, 1397 (2006).
[18] J. He, F. Chen, P. Liddell, and et al., Nanotechnology 16, 695 (2005).
[19] Y. Wakayama, K. Ogawa, T. Kubota, H. Suzuki, T. Kamikado, and S. Mashiko, Appl. Phys. Lett. 85, 329 (2004).
[20] S. Yasutomi, T. Morita, Y. Imanishi, and S. Kimura, Science 304, 1944 (2004).
[21] R. Landauer, IBM Journal Res.Dev. 1, 223 (1957).
[22] R. Landauer, Phil.Mag. 21, 863 (1970).
[23] W. Y. Kim and K. S. Kim, J. Comput. Chem. 29, 1073 (2008).
[24] W. Kim, Y. Choi, and K. Kim, J. Mater. Chem. 18, 4510 (2008).
[25] S. Cho, Y.-F. Chen, and M. S. Fuhrerb, Appl. Phys. Lett. 91, 123105 (2007).
[26] T. B. Martins, R. H. Miwa, A. J. R. da Silva, and A. Fazzio, Phys. Rev. Lett. 98, 196803 (2007).
[27] L. Pisani, J. Chan, B. Montanari, and N. Harrison, Phys.Rev.B 75, 064418 (2007).
[28] M. Galperin and A. Nitzan, Phys. Rev. Lett. 95, 206802 (2005).
[29] M. Galperin and A. Nitzan, J. Chem. Phys. 124, 234709 (2006).
[30] M. Galperin, A. Nitzan, and M. Ratner, Phys.Rev.B. 74, 075326 (2006).
[31] M. Büttiker, Y. Imry, R. Landauer, and S. Pinhas, Phys. Rev. B 31, 6207 (1985).
[32] M. Büttiker, Phys. Rev. Lett. 57, 1761 (1986).
[33] Z. Vager and R. Naaman, Chem.Phys. 281, 305 (2002).
[34] M. Brandbyge, J. L. Mozos, P. Ordejon, J. Taylor, and K. Stokbro, Phys. Rev. B 65, 165401 (2002).
[35] B. Larade, J. Taylor, H. Mehrez, and H. Guo, Phys.Rev.B 64, 075420 (2001).
[36] M. Bixon and J. Jortner, Adv. Chem. Phys. 106, 35 (1999).
[37] A. Nitzan, M. Galperin, G. Ingold, and H. Grabert, J.Chem.Phys. 117, 10837 (2002).
[38] A. Nitzan, J. Jortner, J.Wilkie, A. Burin, and M. Ratner, J.Phys.Chem.B 104, 5661 (2000).
[39] A. Nitzan, Annu. Rev. Phys. Chem. **52**, 681 (2001).
[40] L. Caron, G. Peruzzo, G. Bader, and L. Sanche, Phys. Rev. B **33**, 3027 (1986).
[41] B. D. Fainberg, M. Jouravlev, and A. Nitzan, Phys. Rev. B **76**, 245329 (2007).
[42] J. Lehmann, S. Camalet, S. Kohler, and P. Hanggi, Chem. Phys. Lett. **368**, 282 (2003).
[43] F. Keilmann and R. Hillenbrand, Phil. Trans. R. Soc. Lond. A **362**, 787 (2004).
[44] N. S. Wingreen and Y. Meir, Phys. Rev. B **49**, 11040 (1994).
[45] P. Anderson, Phys. Rev. **124**, 6104 (41).
[46] G. D. Mahan, *Many-particle physics* (Plenum Press, New York, 1990).
[47] L. P. Kadanoff, *Statistical physics. Statics, Dynamics and Renormalization* (Singapore, World Scientific, 2000).
[48] L. Kadanoff, Phys. Rev. **188**, 859 (1969).
[49] G. Göppert, Y. M. Galperin, B. L. Altshuler, and H. Grabert, Phys. Rev. B **66**, 195328 (2002).
[50] H. Imamura, N. Kobayashi, S. Takahashi, and S. Maekawa, Phys. Rev. Lett. **84**, 1003 (2000).
[51] A. Nitzan, *Chemical Dynamics in Condensed Phases. Relaxation, Transfer and Reaction in Condensed Molecular Systems* (Oxford University Press, 2006).
[52] P. Wolfe, W. Brenig, and W. Gotze, Z. Phys. **235**, 59 (1970).
[53] H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics* (Springer, New York, 1982).
[54] O. Berman and S. Mukamel, Phys. Phys. B. **69**, 155430 (2004).
[55] S. Welack, M. Schreiber, and U. Kleinekathofer, J. Chem. Phys. **124**, 044712 (2006).
[56] M. Lindberg and S. W. Koch, Phys. Rev. B **38**, 3342 (1988).
[57] I. I. Rabi, Phys. Rev. **51**, 652 (1937).
[58] D. B. Tran Thoai and H. Haug, Phys. Rev. B **47**, 3574 (1993).
[59] J. Schilp, T. Kuhn, and G. Mahler, Phys. Rev. B **50**, 5435 (1994).
[60] J. Schilp, T. Kuhn, and G. Mahler, Phys. Stat. Sol. **188**, 417 (1995).
[61] S. Butscher, J. Forstner, I. Waldfmuller, and A. Knorr, Phys. Rev. B **72**, 045314 (2005).
[62] L. Allen and J.-H. Eberly, *Optical resonance and two-level atoms* (John Wiley & Sons, New York, 1997).
[63] T. H. Stievater, X. Li, D. G. Steel, D. Gammon, D. S. Katzer, D. Park, C. Piermarocchi, and L. J. Sham, Phys. Rev. Lett. **87**, 133603 (2001).
[64] H. Kamada, H. Gotoh, J. Temmyo, T. Takagahara, and H. Ando, Phys. Rev. Lett. **87**, 246401
[65] H. Htoon, T. Takagahara, D. Kulik, O. Baklenov, J. A. L. Holmes, and C. K. Shih, Phys. Rev. Lett. 88, 087401 (2001).

[66] A. Zrenner, E. Beham, S. Stuffer, F. Findeis, M. Bichler, and G. Abstreiter, Nature 418, 612 (2002).

[67] B. W. Shore, K. Bergmann, A. Kuhn, S. Schiemann, J. Oreg, and J. H. Eberly, Phys. Rev. A 45, 5297 (1992).

[68] J. S. Melinger, S. R. Gandhi, A. Hariharan, D. Goswami, and W. S. Warren, J. Chem. Phys. 101, 6439 (1994).

[69] E. B. Treacy, Phys. Lett. A 27, 421 (1968).

[70] N. V. Vitanov, T. Halfmann, B. W. Shore, and K. Bergmann, Annu. Rev. Phys. Chem. 52, 763 (2001).

[71] B. D. Fainberg and V. A. Gorbunov, J. Chem. Phys. 121, 8748 (2004).

[72] B. D. Fainberg, B. Levinsky, and V. A. Gorbunov, J. Opt. Soc. Am. B 22, 2715 (2005).

[73] B. D. Fainberg, J. Chem. Phys. 109, 4523 (1998).

[74] F. Wang and Y. R. Shen, Phys. Rev. Lett. 97, 206806 (2006).

[75] T. Brixner, F. J. G. de Abajo, J. Schneider, C. Spindler, and W. Pfeiffer, Phys. Rev. B 73, 125437 (2006).

[76] V. M. Akulin and W. P. Schleich, Phys. Rev. A 46, 4110 (1992).

[77] H. Petek and S. Ogawa, Progress in Surface Science 56, 239 (1997).

[78] M. Galperin, M. A. Ratner, and A. Nitzan, J. Phys.: Condens. Matter 19, 103201 (2007).