Stochastic Schrödinger equation for hot-carrier dynamics in plasmonic systems

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We present a multiscale method coupling the theory of open quantum systems with real-time ab initio treatment of electronic structures to study hot-carrier dynamics in photoexcited plasmonic systems. We combine the Markovian Stochastic Schrödinger equation (SSE) with a first-principle description of the electronic degrees of freedom of a molecular moiety absorbed on a metallic nanoparticle, the latter modelled classically according to the polarizable continuum model. Pure dephasing and relaxation channels are defined within SSE. We apply this methodology to study the effect of relaxation (T_1) and pure dephasing (T_2) times on the hot-carrier dynamics in a system composed of CHO adsorbed on a vertex of a rhodium nanocube and irradiated with a 2.7 eV light pulse, inspired by the experimental results on plasmon-driven CO_2 photoreduction. The results highlight in particular that a charge injection retarded with respect to the laser pulse is based on coherence effects.

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I. INTRODUCTION

Achieving fine control of light-matter interaction at the nanoscale could lead to great advances in many technological fields such as sensing, communication, medicine, catalysis and renewable energy.[1–5] In this sense, metallic nanoparticles (NPs) are particularly promising as they can efficiently absorb and confine electromagnetic radiation by activating the Localized Surface Plasmon Resonances (LSPRs).[6,7] As it decays, the energy stored in the LSPRs promotes the generation of electron-hole pairs which then separately thermalize, reaching a high-temperature equilibrium Fermi-Dirac distribution, as if the carriers (electron and holes) were heated up.[8–16] Before they relax back to the lattice-temperature distribution through phonon scattering, these hot carriers (HCs) can be exploited to drive chemical reactions on the NP surface and this possibility provides a rationale for effective light-to-chemical energy conversion.[17–23] Despite the great interest this mechanism has collected in the past 15 years, its complexity has prevented the design of a complete and coherent framework for HCs mediated reactions to date. Such a phenomenon indeed involves multiple interacting species, namely the reacting molecules, NP, HCs and the external radiation. The dynamics and the interplay between those actors are intrinsically quantum, as the driven catalysis might be promoted by different quantum mechanisms such as HCs transfer, excited state dynamics, near-field enhanced intramolecular transitions, population of vibrational states, and carriers-phonon scattering.[24–31] In order to deal with such a complex picture, we developed a multiscale model that is able to properly treat the real-time dynamics of electrons in a molecular moiety absorbed on an optically excited NP,[32–36] encompassing continuum electrodynamics, Density Functional Theory (DFT) and post-DFT approaches such as GW coupled to Bethe-Salpeter Equation (BSE). We recently applied this model to the study of rhodium-catalyzed CO_2 reduction.[37] Indeed, it was shown how Rh nanocubes selectively convert CO_2 into CH_4 when illuminated with an external radiation which frequency matches the LSPR on the nanocubes, in a hydrogen-rich environment.[38,39] We demonstrated that the efficiency of the photoexcited reaction resides in a NP-to-molecule hole injection that ease the pathway to CH_4 production by making the CHO fragment's oxygen more reactive. A deeper insight on the microscopic process guiding the injection, showed that the presence of the Rh nanocube promotes such a direct charge transfer due to the enhancement of near field intensity.[37]

Plasmon-mediated HC injection occurs in very short timescales concurrent with dephasing and nonradiative relaxation decays induced by rapid interaction with the surrounding environment.[40–43]

In this framework, the system can no longer be considered close but rather open[44–47], meaning that dephasing and relaxation have to be properly accounted for a comprehensive understanding of the whole phenomena.[48–51] In the theory of open quantum systems, several approaches have been developed.[44,45,52–55] One method is the Lindblad[56,57] master equation for the reduced density matrix,[58–63] which provides a means to solve the problem under the Markovian limit[64–66] (i.e., when the environment relaxes at a faster rate than the system). Alternatively, another approach is rooted in the time evolution of the system wavefunction, known as the stochastic Schrödinger equation (SSE) in the Markovian limit.[55] SSE incorporates environmental interaction through stochastic and dissipative terms in each realization. As the number of trajectories tends to infinity, SSE yields results identical to those by the Lindblad equation[64,67] offering a computational advantage as it reduces the problem size by propagating the wavefunction instead of the density matrix. Among the variety of methods developed to practically solve SSE[68–71], the quantum jump algorithm, where the jumping probability is demanded to a Monte Carlo technique[72,73], has been widely used.[74,75]

SSE can be coupled to a quantum mechanical description of the system of interest[41,76,77], e.g. using at Time-Dependent Density Functional Theory (TDDFT)[70,78–80], Configuration Interaction Singles (CIS) level of theory[73,76], or GW-BSE equation.[37,81,82] Moreover, SSE has been also recently coupled to a multiscale approach, i.e. by using the polarizable continuum model (PCM) to describe the real-time polarization of a metal NP under the influence of an external electromagnetic pulse, in presence of a molecule or a cluster treated at quantum mechanical (QM) level of theory.[33,35,37,73,82] This time-dependent QM/continuum method is dubbed TD-PCM-NP.[35]

In this work, we use the TD-PCM-NP in combination with SSE to study electron/hole dynamics[83–86] in the early steps of plasmon-mediated photoreduction of carbon dioxide on rhodium nanocubes.[87] Specifically, we investigated the effect of pure dephasing and relaxation on the generation of electron and holes in the reaction intermediate CHO, when adsorbed on a rhodium corner, with and without the classical portion of the nanocube. The tool employed to analyze the HCs dynamics is the differential-projected density of states ΔPDOS[86] that provides the time evolution of the molecular orbitals population projected onto the atomic orbitals of a chosen fragment. Proper integration of ΔPDOS over energy provides the time evolution of charge population.

The present work is organized as follows: in Section II we show the theoretical model; computational details are collected in Section III; results are presented and discussed in Section IV, while conclusions are given in Section V.

II. THEORY

A. Stochastic Schrödinger equation

The time-evolution of the electronic wavefunction of the molecular target is modeled by the stochastic Schrödinger equation (SSE). This equation extends the traditional time-dependent Schrödinger equation to account for interactions with an external environment, allowing the treatment of the quantum system as open. SSE[33,73] has been implemented in the TDPlas-WaveT suite[88] within the Markovian limit[64] and it is given by:

$$i\frac{d}{dt}|\Psi_S(t)\rangle = \hat{H}(t)|\Psi_S(t)\rangle + \sum_q^M l_q(t)\hat{S}_q|\Psi_S(t)\rangle - \frac{i}{2}\sum_q^M \hat{S}_q^\dagger \hat{S}_q|\Psi_S(t)\rangle, \tag{1}$$

where the operator $\hat{S}_q$ is representative of the environment effect through the M interaction channels indexed by q. The dissipation induced by the environment is included by the non-Hermitian term $-\frac{i}{2}\sum_q^M \hat{S}_q^\dagger \hat{S}_q$. The fluctuation term $\sum_q^M l_q(t)\hat{S}_q$ is modeled by a Wiener process $l_q(t)$, also generated by the environment. The environment generates population and/or coherence relaxation, depending on the shape of $\hat{S}_q$. The system coincides with the electronic degrees of freedom of the QM portion, affected by the classical NP. Averaging the time-dependent coefficients on the number of independent SSE realizations, populations and coherences of the electronic states can be obtained.[73] The time dependent Hamiltonian $\hat{H}(t)$ includes the electronic field-free Hamiltonian $\hat{H}_0$ and the interaction with the incident pulse, when only the QM system is included:

$$\hat{H}(t) = \hat{H}_0 - \hat{\vec{\mu}} \cdot \vec{F}(t), \tag{2}$$

with $\hat{\vec{\mu}}$ the molecular dipole and $\vec{F(t)}$ the external pulse. The system wavefunction is expanded in the field-free eigenstates of $\hat{H}_0$

$$|\Psi_S(t)\rangle = \sum_\lambda C_\lambda(t)|\lambda\rangle. \tag{3}$$

We included two possible shapes for the operator $\hat{S}_q$ to account for pure dephasing and relaxation. The interaction channel q is here identified with the effect on a $|\lambda\rangle$ state, so we use the definition $\hat{S}_\lambda \equiv \hat{S}_q$.[73] The pure dephasing operator generates a coherence decay, keeping the population untouched. It is defined as[73]

$$\hat{S}_\lambda^{\text{dep}} = \sqrt{\gamma_\lambda/2}\sum_{\lambda'} P(\lambda',\lambda)|\lambda'\rangle\langle\lambda'|, \tag{4}$$

where $P(\lambda',\lambda)$ is equal to -1 if $\lambda' = \lambda$ or equal to 1 otherwise. Dephasing time T_2 is equal to the inverse of γ_λ, which is given as a phenomenological parameter. Since γ_λ is the same for any state pair, $T_2 = \frac{1}{\gamma}$.

On the other hand, the relaxation accounts for population decay through nonradiative pathways. Here we propose a relaxation operator based on the well-known energy gap law[89–97], defined as

$$\hat{S}_\lambda^{\text{nonr}} = \sqrt{\Gamma_\lambda}|\lambda-1\rangle\langle\lambda| \tag{5}$$

with

$$\Gamma_\lambda = \alpha \exp\left[-\frac{\Delta E_\lambda}{\omega_v}\right], \tag{6}$$

where ΔE_λ ($\lambda > 0$) is the energy difference between $|\lambda\rangle$ and $|\lambda-1\rangle$ adjacent electronic states, ω_v is the vibrational frequency which mediates relaxation between adjacent states, and α is a constant. Subsequently, we will refer to $T_1 = \frac{1}{\alpha}$, which actually represents a lower limit to the T_1 resulting from Eq. 6. The energy gap law defines the rate of nonradiative decay between two electronic states of a molecular system as exponentially dependent on the energy gap ΔE_q.[90,91] The energy gap law is formulated within the assumptions that the electronic excitation is only weakly coupled to the vibrational structure of the molecule, and that the vibronic transition due to the highest frequency vibrational modes serves as the main route for the quantum transition mechanism.

B. TD-PCM-NP

Here, an overview of TD-PCM-NP is provided. More details are available in Refs. 34,35,98. The NP is considered as a continuum system characterized by the polarization charges located in the centre of its surface tesserae. The polarization charges follow the PCM equation in the integral equation formalism (IEF)[98–100] within the boundary element method (BEM) which in frequency domain reads:

$$\mathbf{q}(\omega) = -\mathbf{S}^{-1}\left(2\pi\frac{\varepsilon(\omega)+1}{\varepsilon(\omega)-1}\mathbf{I}+\mathbf{DA}\right)^{-1}(2\pi\mathbf{I}+\mathbf{DA})\,\mathbf{V} = \mathbf{Q}(\omega)\mathbf{V} \tag{7}$$

where $\mathbf{A}$ is a diagonal matrix containing the tesserae areas, the matrices $\mathbf{S}$ and $\mathbf{D}$ are representative of Calderons' projectors and only depends on the geometry of the nanoparticle, $\varepsilon(\omega)$ is the metal dielectric function and $\mathbf{V}$ is the potential generated on the NP surface tesserae by the molecular potential (or by the external field, depending on which polarization is sought for, see below). The

electrodynamics of the NP charges is computed at IEF-BEM level, turning the problem in time domain by Fourier transform of the previous equation[34] as:

$$\mathbf{q}(t) = \int_{-\infty}^{+\infty} dt' \mathbf{Q}(t-t')\mathbf{V}(t'). \tag{8}$$

The time dependent polarization charges enter the equation of the molecular electrodynamics as part of the Hamiltonian in presence of the polarizable NP, which now reads:

$$\hat{H}(t) = \hat{H}_0 - \hat{\vec{\mu}} \cdot \vec{F}(t) + (\mathbf{q}_{ref}(t) + \mathbf{q}_{pol}(t)) \cdot \hat{V}, \tag{9}$$

where $\mathbf{q}_{ref}(t)$ and $\mathbf{q}_{pol}(t)$ are the reflected and polarization charges generated respectively from the interaction with the incident pulse and with the molecular electrostatic potential $\hat{V}$.[32]
In this multiscale case, Eq. 1 is propagated with the Hamiltonian of Eq. 9 and with the system wavefunction defined in the space of the eigenstates of a modified field-free Hamiltonian, accounting for the presence of the NP, as explained in Ref. 82. We couple here the GW-BSE QM description of the reactive part of the system to TD-PCM-NP.[82]

C. Analysis of the hot-carrier dynamics

When analyzing HC dynamics, a very useful tool is the ΔPDOS, introduced in Ref. 86 and applied in Ref. 37. The time-dependent $\Delta\text{PDOS}_K(t,\varepsilon)$ provides a two-dimensional map that displays the population of molecular orbitals, projected onto the atomic orbitals of a chosen fragment K, as a function of time t and energy ε. The subscript K refers to the fragment of the molecular system, defined in the simulations. As an example, in Ref. 86, the intramolecular charge transfer with dipole switching in LiCN has been studies, by defining Li and CN as fragments in ΔPDOS analysis. When integrated over the energy variable, $\Delta\text{PDOS}_K(t,\varepsilon)$ provides the time evolution of the overall electronic population or depopulation (hole population) of a given fragment, allowing to easily assess charge transfer or localization processes. For the single trajectory, i.e. a coherent dynamics, the time dependent ΔPDOS is given by:

$$\begin{aligned}\Delta\text{PDOS}_K(t,\varepsilon) \;=\; & -\sum_{i}^{occ} w_i^K \text{Re}\left[\sum_{\lambda,\lambda'} C_\lambda^*(t) C_{\lambda'}(t) \sum_{a}^{vir} {d_{i,\lambda}^a}^* d_{i,\lambda'}^a\right] L_\eta(\varepsilon - \varepsilon_i) \\ & + \sum_{a}^{vir} w_a^K \text{Re}\left[\sum_{\lambda,\lambda'} C_\lambda^*(t) C_{\lambda'}(t) \sum_{i}^{occ} {d_{i,\lambda}^a}^* d_{i,\lambda'}^a\right] L_\eta(\varepsilon - \varepsilon_a),\end{aligned} \tag{10}$$

where $C_\lambda(t)$ are the time-dependent coefficients of the expansion of the electronic wavefunction in terms of states $|\lambda\rangle$, that are eigenstates of H_0 (see Eq. 3) or of the modified field-free Hamiltonian

with NP[82]. The $|\lambda\rangle$ states are linear combinations of singly excited Slater determinants in which an electron from the occupied state i is promoted to an empty states a, $d^a_{i,\lambda}$ being the coefficients of such expansion. $w^K_{i/a}$ are Lowdin weights. $L_\eta(\varepsilon-\varepsilon_i)$ are Lorentzian functions of center ε_i and width η.

Electron and hole populations generated in the fragment K of the QM system are given by:

$$\text{electron population} = \quad \frac{1}{2}\int_{-\infty}^{\infty}[\Delta\text{PDOS}_K(t,\varepsilon)+|\Delta\text{PDOS}_K(t,\varepsilon)|]\,d\varepsilon \tag{11}$$

$$\text{hole population} = \quad \frac{1}{2}\int_{-\infty}^{\infty}[\Delta\text{PDOS}_K(t,\varepsilon)-|\Delta\text{PDOS}_K(t,\varepsilon)|]\,d\varepsilon. \tag{12}$$

Eqs.11-12 consider any increase in the population of an orbital as electrons generated with respect to the ground state, and any decrease in such population as holes. These equations also apply to ground states with fractional orbital populations and reduce to the standard integration over empty or occupied energy ranges when orbitals are fully empty or fully occupied.

To avoid an explicit double summation over the λ index, it is possible to rewrite Eq. 10, as:

$$\Delta\text{PDOS}^{\text{SSE}}_K(t,\varepsilon) = -\sum_i^{occ} w_i^K z_i(t) L_\eta(\varepsilon-\varepsilon_i) + \sum_a^{vir} w_a^K z_a(t) L_\eta(\varepsilon-\varepsilon_a) \tag{13}$$

where

$$z_i(t) \;=\; \sum_a^{vir} |\sum_\lambda C_\lambda(t) d^a_{i,\lambda}|^2 \tag{14}$$

$$z_a(t) \;=\; \sum_i^{occ} |\sum_\lambda C_\lambda(t) d^a_{i,\lambda}|^2 \tag{15}$$

When analyzing an SSE dynamics the $\overline{C^*_\lambda(t)C_{\lambda'}(t)}$, i.e. the product of the $C^*_\lambda(t)$ coefficients averaged over all the trajectories are in principle needed, namely we need to compute:

$$\begin{aligned}\Delta\text{PDOS}^{\text{SSE}}_K(t,\varepsilon) \;&=\; -\sum_i^{occ} w_i^K \text{Re}\left[\sum_{\lambda,\lambda'}\overline{C^*_\lambda(t)C_{\lambda'}(t)}\sum_a^{vir} {d^a_{i,\lambda}}^* d^a_{i,\lambda'}\right] L_\eta(\varepsilon-\varepsilon_i) \\ &+\; \sum_a^{vir} w_a^K \text{Re}\left[\sum_{\lambda,\lambda'}\overline{C^*_\lambda(t)C_{\lambda'}(t)}\sum_i^{occ} {d^a_{i,\lambda}}^* d^a_{i,\lambda'}\right] L_\eta(\varepsilon-\varepsilon_i) = \\ &=\; -\sum_i^{occ} w_i^K \overline{z_i(t)} L_\eta(\varepsilon-\varepsilon_i) + \sum_a^{vir} w_a^K \overline{z_a(t)} L_\eta(\varepsilon-\varepsilon_a).\end{aligned} \tag{16}$$

Now, if we write $\overline{C^*_\lambda(t)C_{\lambda'}(t)} = \overline{C^*_\lambda(t)}\cdot\overline{C_{\lambda'}(t)} + \Delta_{\lambda\lambda'}(t)$, we can express $\overline{z_i(t)}$ as:

$$\overline{z_i(t)} = \sum_a |\sum_\lambda \overline{C_\lambda(t)^a_{i,\lambda}} d^a_{i,\lambda}|^2 + \Delta_i(t) \tag{17}$$

with $\Delta_i(t) = \sum_a \sum_{\lambda\lambda'}(t)\Delta_{\lambda\lambda'}(t) d^{a*}_{i,\lambda'} d^a_{i\lambda}$. A similar expression holds for $\overline{z_a(t)}$.

In this way we obtain for the full SSE case:

$$\begin{aligned}\Delta\mathrm{PDOS}^{\mathrm{SSE}}_K(t,\varepsilon) \;=\; & -\sum_i^{occ} w_i^K \mathrm{Re}\left[\sum_{\lambda,\lambda'} \overline{C^*_\lambda(t)}\cdot\overline{C_{\lambda'}(t)} \sum_a^{vir} d^a_{i,\lambda}{}^* d^a_{i,\lambda'}\right] L_\eta(\varepsilon-\varepsilon_i) \\ & + \sum_a^{vir} w_a^K \mathrm{Re}\left[\sum_{\lambda,\lambda'} \overline{C^*_\lambda(t)}\cdot\overline{C_{\lambda'}(t)} \sum_i^{occ} d^a_{i,\lambda}{}^* d^a_{i,\lambda'}\right] L_\eta(\varepsilon-\varepsilon_i) + \mathscr{D}^k(t)\end{aligned} \tag{18}$$

Where $\mathscr{D}^k(t) = -\sum_i^{occ} w_i^K \Delta_i(t) L_\eta(\varepsilon-\varepsilon_i) + \sum_a^{vir} w_a^K \Delta_a(t) L_\eta(\varepsilon-\varepsilon_a)$. Interestingly, because the terms $\Delta_{\lambda\lambda'}(t)$ represent the covariance of the products $C^*_\lambda(t)C_{\lambda'}(t)$, their contribution to the $\Delta\mathrm{PDOS}^{\mathrm{SSE}}_K(t,\varepsilon)$ given by $\mathscr{D}^k(t)$ might provide information on how much the trajectories are correlated.

III. COMPUTATIONAL DETAILS

We employed a multiscale approach to account for an extended Rh nanocube of 37 nm edge coupled with an atomistic cluster made by 19 Rh atoms positioned on the corner of the NP bonded to CHO residue.[37] CHO is the reaction intermediate of CH_4 formation, and it has been chosen because its dissociation into CH and O is the rate-determining step in the thermally activated reaction toward CH_4.[101,102] The classical portion has been treated with TD-PCM-NP. A representation of the simulate systems is reported in Figure 1 where the bare quantum (QM) system (panel a) or the whole QM/classical system (panel b) interacts with the pulse.

The preparation of the computational system including geometry optimization and excited state calculations has been described in Ref. 37. For the sake of the reader, we repeat here the details. The atomistic structure of Rh_{19} has been extracted from a Rh(111) slab optimized at DFT level with Quantum Espresso, version 6.3.[103,104] We used a plane waves basis set and PBE functional while the core-electrons were modelled with the Optimized Norm-Conserving Vanderbilt pseudopotential[105] and the energy cut-off for the basis set expansion was set to 1080 eV. The system's geometry was optimized using a 8x8x1 k-point grid, with an additional 20 Å vacuum layer added perpendicular to the surface direction to prevent the formation of spurious electric fields.[106] While keeping the two bottom layers fixed in their ideal bulk positions, all other atoms were relaxed utilizing the Broyden–Fletcher–Goldfarb–Shanno quasi-Newton algorithm[107] until the residual forces fell below 10^{-4} eV/Å. Convergence was achieved with a threshold of 10^{-9} eV

for the ground state total energy. Rh_{19} was extracted from the two outermost layers of the slab and employed as a substrate for the geometry optimization of CHO species performed with DFT at PBE/DZ level of theory by means of AMS code.[108] 455 electronic states have been employed in the electron dynamics calculation.

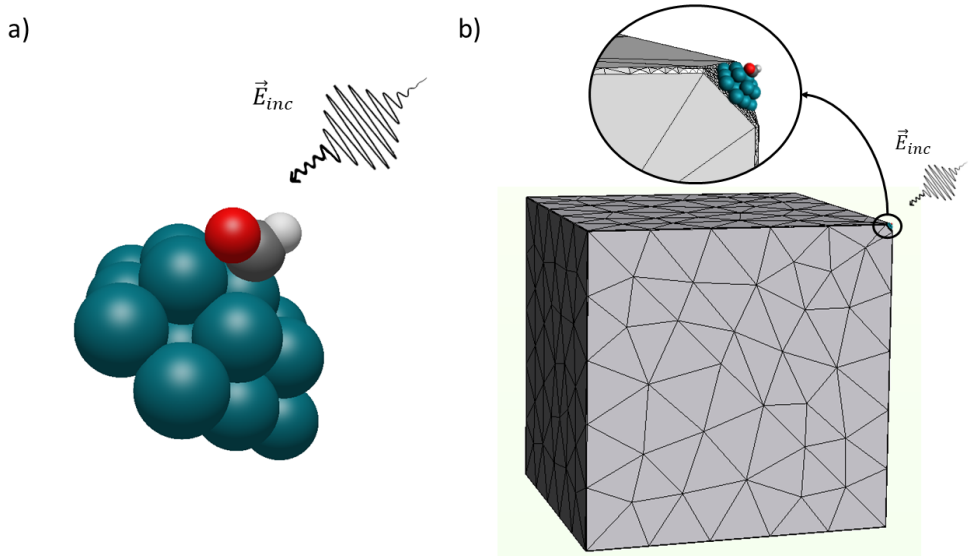

FIG. 1. a) Representation of the QM system Rh_{19}-CHO interacting with the incident electric field. b) Representation of the QM system coupled with the Rh nanocube.

Electron dynamics, with and without the classical NP, have been carried out with the WaveT-TDPlas code.[35,98] We have employed a Gaussian envelope function for the time-dependent external field:

$$\vec{\mathrm{F}}(t) = \vec{\mathrm{F}}_{\max} \exp\left[-\frac{(t-t_0)^2}{2\sigma^2}\right] \sin(\omega t), \tag{19}$$

where $\vec{\mathrm{F}}_{\max}$ is the field amplitude (the intensity I_{max} is equal to $\frac{1}{2}|\vec{\mathrm{F}}_{\max}|^2$), t_0 and σ are the centre and the amplitude of the Gaussian respectively, and ω is the pulse frequency. We employed a 459 nm as pulse wavelength, with FWHM equal to 23 fs and intensity $I_{max} = 3.3 \times 10^4$ W/cm^2, linearly polarized perpendicular to the vertex of the nanocube. A second-order Euler algorithm[32] was used to propagate Eq. 1. We simulated 100 fs with a time step of 1.21 as. 768 SSE trajectories have been carried out for each condition of dephasing and relaxation considered. MPI parallel protocol has been used, with one SSE trajectory per MPI process. Performance of our MPI implementation is reported in Supporting Information (SI) as weak and strong scaling on a model system composed

of LiCN (500 excited states) as QM system and a spherical gold NP (370 tesserae).

A homemade Fortran90 code has been used to compute the ΔPDOS and its integral in order to compute electron and hole populations. The amplitude of the Lorentzian function is 0.0272 eV and the energy grid used to compute ΔPDOS and its integration goes from -21.7 eV to 21.7 eV with a step of 0.0217 eV. The post-processing calculation has been performed considering two fragments (CHO and all rhodium atoms).

IV. RESULTS AND DISCUSSION

This section presents the key findings derived from our simulations, aimed to show the effects

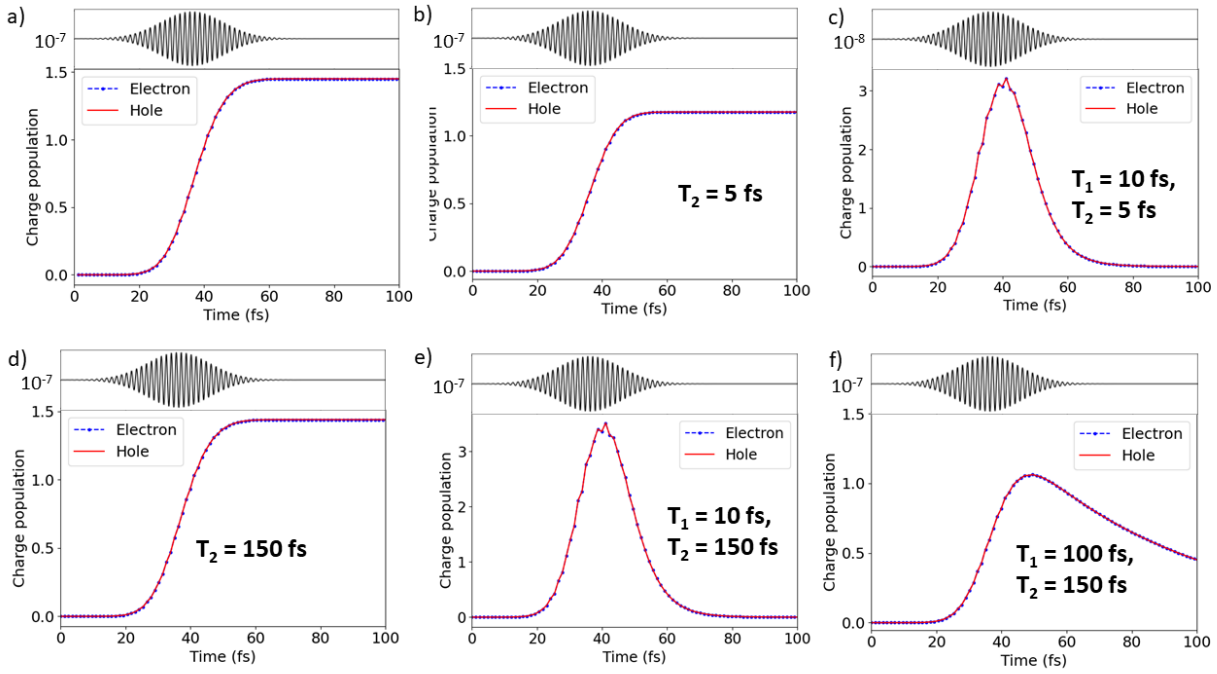

FIG. 2. Time-evolution of the photoinduced charge carrier populations (electron and hole) in the quantum part (Rh_{19} - CHO) in presence of different dephasing and relaxation conditions: a) without relaxation or dephasing, b) in presence of dephasing only with T_2 = 5 fs, c) including dephasing with T_2 = 5 fs and relaxation with T_1 = 10 fs, d) in presence of only dephasing with T_2 = 150 fs, e) including dephasing with T_2 = 150 fs and relaxation with T_1 = 10 fs and f) including dephasing with T_2 = 150 fs and relaxation with T_1 = 100 fs.

of the relaxation and pure dephasing on the charge population in the systems reported in Figure 1. After performing the electronic dynamics of the QM system (in absence of the continuum NP, Figure 1a), the wavefunction coefficients were used to compute the ΔPDOS and the electron and hole populations in the whole system.

In this case, the total ΔPDOS, i.e. using the orginal nonprojected density of states (no fragment is defined), has been used in Eqs. 11-12. Figure 2 illustrates the temporal evolution of absolute hole and electron populations under various dephasing and relaxation conditions. The maximum charge population is generated when dephasing or relaxation events are absent (panel a), i.e. for a coherent dynamics. A similar result is obtained in presence of slow dephasing decay, such as in panel d) with T_2 = 150 fs when the dephasing process has a longer timescale than the electric field duration. The charge population has a flat profile when no relaxation decay is included, which highlights that populations weight more than coherences in the calculation of time changes of ΔPDOS, as in Eq. 16. The effect of coherence decay, induced by pure dephasing, is indicated by a decreasing on the maximum charge population generated, which is much more evident with fast dephasing time (panel b). On the other hand, when both dephasing and relaxation channels are incorporated into the model, as shown in panels c), e) and f), the charge population decreases over time, with a decay rate determined by the relaxation time T_1. Moreover, the charge population generated decreases when fast relaxation is considered. It becomes evident that when relaxation processes occur within the timescale of HC generation, i.e. $\sim$ 10 fs, is essential to include them in the modeling to achieve an accurate simulation of a realistic system.

Furthermore, the relative electron and hole population were computed, dividing the QM portion into two fragments: the reaction intermediate CHO and the rhodium atoms. In Figure 3 the charge population percentage on CHO fragment has been reported as a function of time for different simulation conditions. The charge population percentage is obtained, dividing the electron (hole) population by the maximum electron (hole) population generated in the whole system (Rh_{19}-CHO) during the dynamics. The net charge, computed as the difference between hole and electron charges, is also shown. In any case, the hole injection mechanism on the CHO fragment prevails, as already highlighted in ref. 37. The charge population percentage reported in panel a) is computed in the absence of dephasing or relaxation, resulting in a steady charge population without an overall decrease. The hole population shows two maxima: one right after the interaction

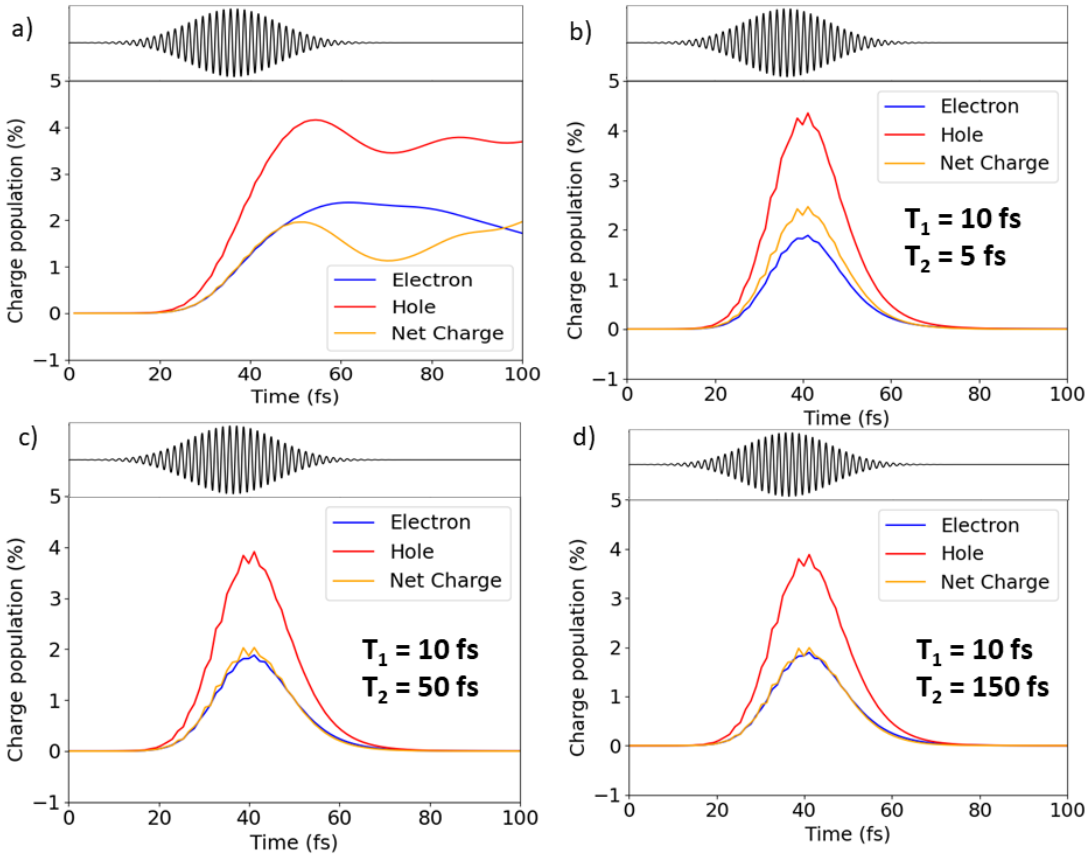

FIG. 3. a) Time-evolution of the photoinduced charge carrier population into CHO (%) in absence of dephasing or relaxation. Time-evolution of the photoinduced charge carrier population into CHO (%) in presence of relaxation with T_1 = 10 fs and different values of dephasing: b) T_2 = 5 fs, c) T_2 = 50 fs, d) T_2 = 150 fs.

with the incident peaks and another after 80 fs, suggesting a two-step hole injection mechanism.[37]

The effect of a relaxation time T_1 = 10 fs combined with different dephasing time is shown in panels b)-d). The rapid relaxation mechanism manifests as a charge population decay right after the end of the interaction with the incident pulse and small peaks in correspondence to the maximum, attributed to the swift depopulation and repopulation of states. The only observable difference induced by varying the dephasing time appears on the hole population percentage, which is slightly higher with faster dephasing time.

We have analysed the time evolution of charge population percentages with dephasing times T_2 = 5 fs in Figure 4 and T_2 = 150 fs in Figure 5 and varying relaxation time. Including a fast dephasing time, charge population oscillations visible in the coherent dynamics are not present, thus

the second hole injection mechanism, not induced by the electric field, is produced by long-lived coherences. This is important as it shows that an indirect (or better: retarded) charge-injection may exist still based on the coherent evolution of the wavefunction, different from the incoherent indirect charge injection mechanism that is usually considered. Moreover, electron population percentage generated is even lower than in absence of dephasing. Preference of hole generation on CHO, rather than electron generation, is slightly improved with fast decoherence mechanism, although including a decoherence mechanism is not crucial for the realization of the process. The impact of including and varying the relaxation time is manifested as charge population decay after the interaction with the incident field with the rate of relaxation process.

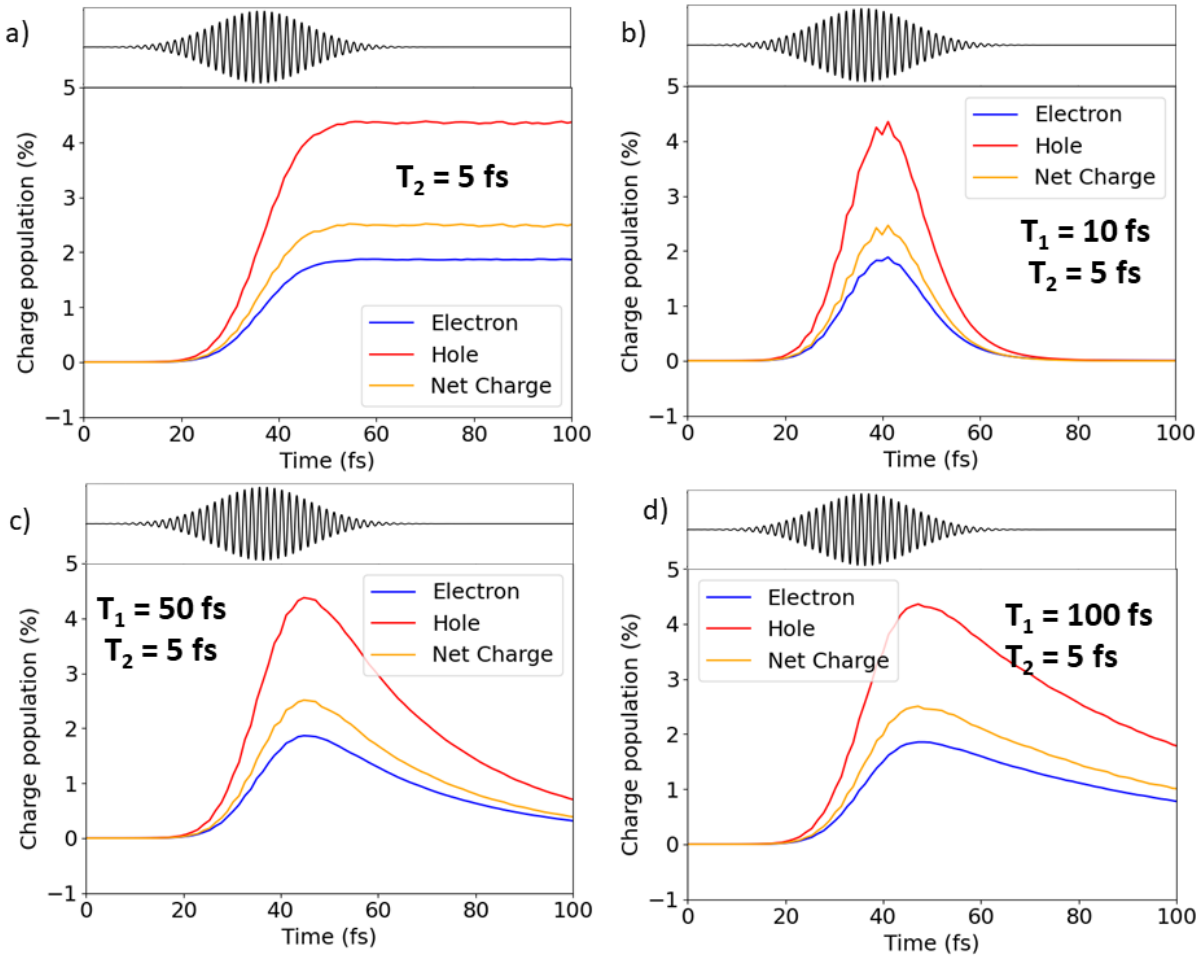

FIG. 4. Time-evolution of the photoinduced charge carrier population into CHO (%) in presence of dephasing with T_2 = 5 fs without including relaxation (a) and including different values of relaxation : b) T_1 = 10 fs, c) T_1 = 50 fs, d) T_1 = 100 fs.

On the other hand, when slower dephasing time is included (T_2 = 150 fs, panel a) of Figure 5) the charge population percentage dynamics approaches the coherent case (figure 2a) in which the hole population percentage achieves two maxima. The results of calculations performed with different relaxation times in panels b)-d) of Figure 5 show a decay profile determined by the T_1 employed. They are very similar to panels b)-d) of Figure 4 obtained with faster dephasing time, but for the maximum charge population percentage, which is slightly lower in this case.

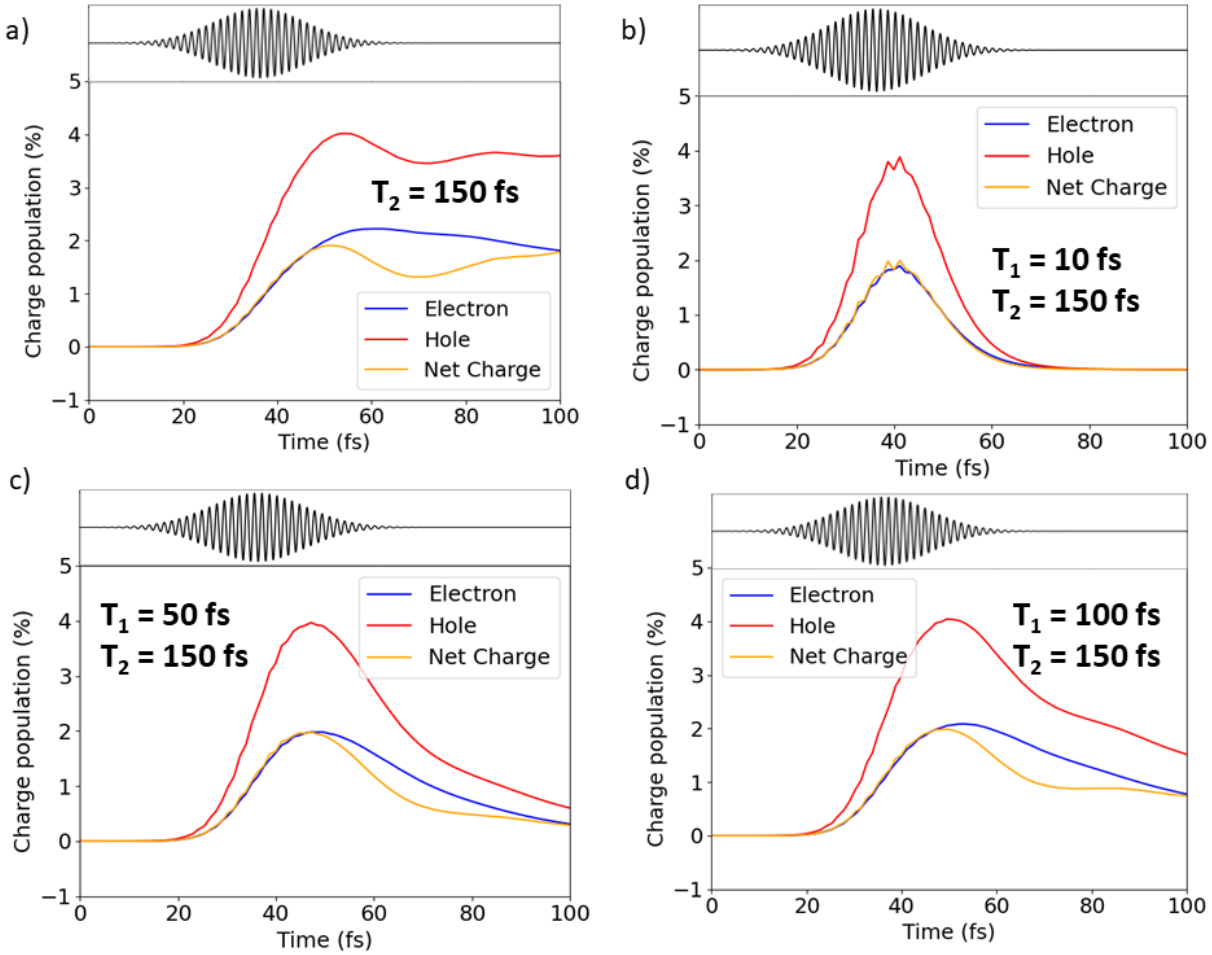

FIG. 5. Time-evolution of the photoinduced charge carrier population into CHO (%) in presence of dephasing with T_2 = 150 fs without including relaxation (a) and including different values of relaxation : b) T_1 = 10 fs, c) T_1 = 50 fs, d) T_1 = 100 fs.

Finally, simulations have also been performed, including the classically described NP as a continuum (Figure 1b). In Figure 6, we report two cases in which both decay processes have been included in the description. A noteworthy observation is that when the classical NP is included, the overall charge population generated is at least two orders of magnitude higher compared to calculations carried out without it (shown in figure 1). Similarly to the scenario without the classical NP, the presence of the smaller relaxation time T_1 = 50 fs (panel a) results in a lower charge population that decays more rapidly compared to the case with T_1 = 100 fs (panel b).

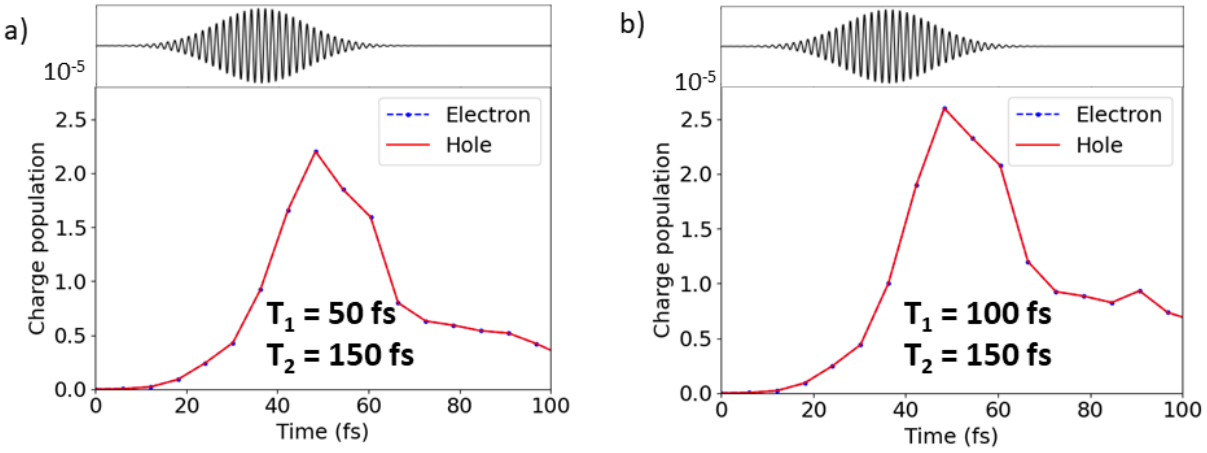

FIG. 6. Time-evolution of the photoinduced charge carrier population into CHO-Rh_{19} system in multiscale calculation when the quantum system is coupled with the classical rhodium nanocube, in presence of dephasing with T_2 = 150 fs and relaxation with T_1 = 50 fs (a), including dephasing with T_2 = 150 fs and relaxation with T_1 = 100 fs (b). Electron and hole populations are superimposed as the system is neutral.

Results with the full system of Figure 1b agree well with literature estimations of HC generation rate and incident photon conversion efficiency.[37]

V. CONCLUSIONS

We present here a real-time multiscale approach to study the HC dynamics in complex systems using SSE for describing environmental effects. Taking inspiration from the experimental photoreduction of carbon dioxide on rhodium nanocubes[38], we defined a QM model composed of two rhodium layers mimicking the nanocube corner, and the CHO reaction intermediate adsorbed on it.

The full system, also including the classical part of the nanocube, is described using the TD-PCM-NP approach. Our real-time (multiscale) approach provided electron and hole population on CHO and rhodium layers. The effect of the pure dephasing is to lower the maximum value of the charge population and to suppress indirect hole injection, in the simulations where the latter were present. Such a result points to the possibility of an indirect, but still coherent, charge injection that is different from what has been identified so far; it is probably better to use the term retarded coherent charge injection for this new mechanism. Simulating a nonradiative decay, via a relaxation time T_1 defined within the energy-gap law, produces a rapid decrease of the charge population. Including the continuum NP in the description determines the enhancement of charge population generated by two order of magnitude, as obtained also in previous calculations.[37] The approach developed allowed to include relaxation and dephasing decay mechanisms that profoundly affects the charge population dynamics, in order to fill the gap with a realistic fast HC dynamics occurring under the influence of external and plasmonic fields.

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SUPPORTING INFORMATION

Weak and strong scaling for SSE parallel calculations.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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