

Real-Time Density Functional Tight Binding: A New Computational Tool for Probing Electronic Properties of Plasmonic Systems

Niranjan V. Ilawe and Bryan M. Wong

Department of Chemical & Environmental Engineering and Materials Science & Engineering Program
University of California - Riverside, Riverside, CA, USA
bryan.wong@ucr.edu

ABSTRACT

Using large-scale, real-time, quantum dynamics calculations, we present a detailed analysis of electronic excitation transfer (EET) mechanisms in a multiparticle plasmonic nanoantenna system. Specifically, we utilize a real-time, time-dependent, density functional tight binding (RT-TDDFTB) approach to provide a quantum-mechanical description (at an electronic/atomistic level of detail) for characterizing and analyzing these systems, without recourse to classical approximations. We also demonstrate highly long-range electronic couplings in these complex systems and find that the range of these couplings is more than twice the conventional cutoff limit considered by Förster resonance energy transfer (FRET)-based approaches. Furthermore, we attribute these unusually long-ranged electronic couplings to the coherent oscillations of conduction electrons in plasmonic nanoparticles. This long-range nature of plasmonic interactions has important ramifications for EET; in particular, we show that the commonly used “nearest-neighbor” FRET model is inadequate for accurately characterizing EET even in simple plasmonic antenna systems. These findings provide a real-time, quantum-mechanical perspective for understanding EET mechanisms and provide guidance in enhancing plasmonic properties in artificial light-harvesting systems.

Keywords: quantum simulations, plasmonic excitations, electronic excitation transfer, real-time electron dynamics, density functional tight binding

1 INTRODUCTION

The efficient harvesting of abundantly available solar energy for enhancing photochemical reactions relies on the efficient capture of photons and subsequent transfer of this excitation energy to the reactive site. Taking inspiration from natural light-harvesting complexes, researchers have begun exploring novel plasmonic antenna systems for directing and controlling this flow of excitation energy.[1] These excitation energy transfer mechanisms are mediated by local surface plasmonic resonances [2] (LSPRs) that describe the coherent oscillation of metal conduction electrons caused by the electric field of the incident photons. These LSPRs are characterized

by a strong optical absorption and large electric field enhancements that are highly dependent on the nanoparticle (NP) material, size, shape, and surrounding environment. Moreover, due to the coherent nature of these oscillating electrons, LSPRs also exhibit large dipole moments, enabling electronic excitation transfer (EET) to neighboring nanoparticles via electrostatic coupling.[3] This electrostatic coupling is analogous to Förster resonance energy transfer (FRET)[4] mechanisms seen ubiquitously in nature, and these strongly-coupled plasmonic nanoparticles have allowed several advances in plasmon-mediated excitation energy transfer processes. In particular, studies by Maier et al., have shown direct experimental evidence of EET along a plasmon waveguide made up of silver nanorods.[3] EET has also been observed in noble materials such as gold and silver nanoclusters which function as acceptors for EET. Recently, Scholes and co-workers[1] have characterized plasmonic nanoantenna systems, inspired from naturally found light-harvesting systems, for use in solar fuel production.

The most widely employed approaches for analyzing EET in the previously mentioned systems are Förster’s approach and classical electrodynamics theories based on solving Maxwell’s equations.[5] However, these models contain approximations, such as spectral overlap or the dipole approximation, which limit their applicability to more complex systems. Some of these concerns have been resolved in recent years by fascinating studies, such as transition densities obtained directly through quantum-chemical calculations and variants such as distributed monopoles, line dipole approximations, and generalizations of Förster’s theory. Nevertheless, as we approach new emerging areas in mesoscale processes, we must re-assess the potential limitations of these simplistic models which may be inapplicable to large, strongly-interacting, electronic systems such as plasmonic nanoantennas.

2 DENSITY FUNCTIONAL TIGHT BINDING

DFTB is an application of the tight-binding (TB) approach to parameterize full DFT.[6] The main idea behind this method is to describe the Hamiltonian ei-

genstates with an atomic-like basis set and replace the Hamiltonian with parameterized matrix elements that depend only on the internuclear distances (neglecting integrals of more than two centers) and orbital symmetries. The expression for the SCC-DFTB total energy is as follows,

$$E_{DFTB} = \sum_i^{occ} \langle \Psi_i | \hat{H}^0 | \Psi_i \rangle + \frac{1}{2} \sum_{AB}^M \gamma_{AB} \delta q_A \delta q_B + E_{rep} \quad (1)$$

where \hat{H}^0 is the Hamiltonian whose matrix elements are explicitly calculated using analytical functions as per the LCAO (linear combination of atomic orbitals) formalism. γ_{AB} is a function of interatomic separation and $\delta q = q_A - q_A^0$ is the difference between the charge of the isolated atom q_A^0 and the charge q_A obtained via a Mulliken population analysis of atom A in the molecule. E_{rep} is the distance-dependent diatomic repulsive potential. It contains the core electron effects, ion-ion repulsion terms as well as some exchange-correlation effects. These pair-wise repulsive functions are obtained by fitting to DFT calculations using a suitable reference structure. The final DFTB Hamiltonian is given by,

$$\hat{H}_{DFTB} = \langle \varphi_\mu | \hat{H}_0 | \varphi_\nu \rangle + \frac{1}{2} \hat{S}_{\mu\nu} \sum_X^M (\gamma_{AX} + \gamma_{BX}) \Delta q_X \quad (2)$$

2.1 Real-Time Time-Dependent DFTB

For the quantum dynamics calculations, the real-time, time-dependent DFTB (RT-TDDFTB) approach is utilized to propagate the one electron density matrix in the presence of external time-varying electric fields to obtain the time-dependent EET response of the system according to the Liouville von Neumann equation of motion which, in the nonorthogonal-DFTB basis, is given by

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{1}{i\hbar} [S^{-1} \cdot \hat{H}[\hat{\rho}] \cdot \hat{\rho} - \hat{\rho} \cdot \hat{H}[\hat{\rho}] \cdot S^{-1}] \quad (3)$$

3 RESULTS

Before proceeding to a detailed analysis of the EET mechanism in plasmonic nanoantenna systems, we first characterize the LSPR of a single plasmonic NP. Accordingly, we plot the absorption spectrum of a single icosahedral shaped sodium NP (Na_{55}), containing 55 atoms and a diameter of 13 Å, using our RT-TDDFTB methodology. As shown in Figure 1, a prominent peak, which corresponds to the LSPR, is seen around 3.16 eV and is in agreement with previously published computational[7] and experimental results.[8]

With the plasmon energy of a single NP fully characterized, we next turn our attention to a multi-particle

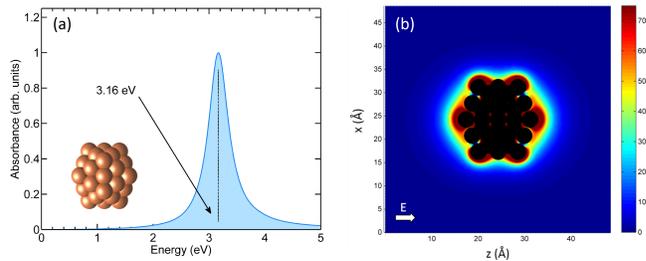


Figure 1: (a) Absorption spectra of the Na_{55} NP (inset) calculated using RT-TDDFTB. The plasmon energy peak is observed at 3.16 eV; (b) Electric field enhancement of the Na_{55} NP distributed in a dipolar fashion in alignment with polarization vector \mathbf{E} . The dark spheres in (b) indicate the position of the Na atoms in the Na_{55} NP.

plasmonic nanoantenna composed of 4 identical Na_{55} NPs as shown in Figure 2. The inter-particle distance (center to center) is set to 73 Å, and each NP is oriented with its transition dipole moment aligned in the z-direction. We excite only NP1 using a laser with its energy tuned to the single Na_{55} NP plasmon energy and polarized in the z-direction. Figure 2 plots the time-dependent dipole moments induced in all of the NPs within the nanoantenna system. The RT-TDDFTB calculations predict substantial dipole moments being induced in all of the NPs, indicating EET from the excited NP1 to the remaining NPs along the nanoantenna, corroborating previous experimental observations of EET observed in a chain of metallic NPs.[3]

3.1 Two-Level System Model for the Four NP System (Including only Nearest-Neighbor Interactions)

While our RT-TDDFTB calculations fully incorporate electronic and atomistic details to characterize EET in this plasmonic donor-acceptor pair, to obtain deeper mechanistic insight into this complex quantum dynamical process, we formulate an analytical model based on a two level system (TLS) to highlight the basic physics that mediate interactions between the NP pair. This model is based on previous work on EET mechanisms between photosynthetic pigments.[9] From linear response theory,[10] and considering each NP as a TLS, we can obtain closed-form analytical expressions of the expectation values of the dipole moment. Furthermore, to expand the TLS model to capture the EET dynamics beyond the second NP, we first approximate the interactions between the various NPs to be limited to only nearest neighbor interactions. For instance, NP2 is only stimulated via oscillations in NP1, NP3 only due to NP2, and so on. This approximation is a commonly used assumption used in many classical electrodynamic approaches and is also based on the maximum cutoff dis-

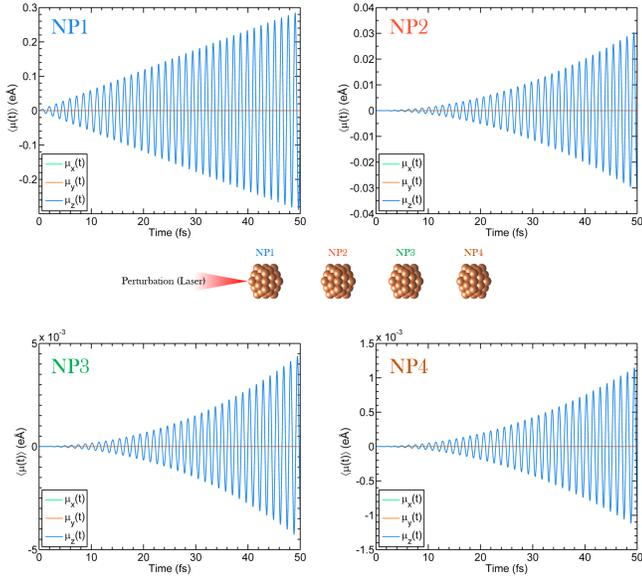


Figure 2: Time-dependent dipole moments induced in the four NPs of the plasmonic nanoantenna system upon optical excitation of NP1 with a sinusoidal electric field perturbation calculated using RT-TDDFTB. The induced dipole moments in the NPs are indicative of the electronic excitation transfer in the multi-particle plasmonic nanosystem.

tance (i.e., 10 nm), considered by FRET approaches[11], beyond which the EET is considered negligible.

$$\mu_1(t) \approx \frac{E_0}{\hbar} |\mu_1|^2 t \cdot \cos(\omega_{PET}) \hat{r}_{PE} \quad (4)$$

$$\mu_2(t) \approx \frac{E_0}{4\pi\epsilon_0 \hbar^2 r^3} |\mu_1|^4 t^2 \sin(\omega_{PET}) \hat{r}_{PE} \quad (5)$$

$$\mu_3(t) \approx \frac{E_0}{24\pi^2 \epsilon_0^2 \hbar^3 r^6} |\mu_1|^6 t^3 \sin(\omega_{PET}) \hat{r}_{PE} \quad (6)$$

$$\mu_4(t) \approx \frac{E_0}{192\pi^3 \epsilon_0^3 \hbar^4 r^9} |\mu_1|^8 t^4 \sin(\omega_{PET}) \hat{r}_{PE} \quad (7)$$

We denote Eqs. 4, 5, 6, and 7 as the TLS model; the details of which can be found in Ref.[12]

Figure 3 compares the dipole moments calculated using the TLS model with the RT-TDDFTB results. While the results of our analytical TLS model match closely with the RT-TDDFTB results for NP1 and NP2, it grossly underestimates the dipole oscillations in NP3 and NP4. The failure of the analytical model indicates that the “nearest-neighbor” approximation considered in the multi-particle model is the culprit. To prove this conjecture, we modify the TLS model to include interactions between all the NPs in the entire nanoantenna. For example, NP4 is stimulated collectively by

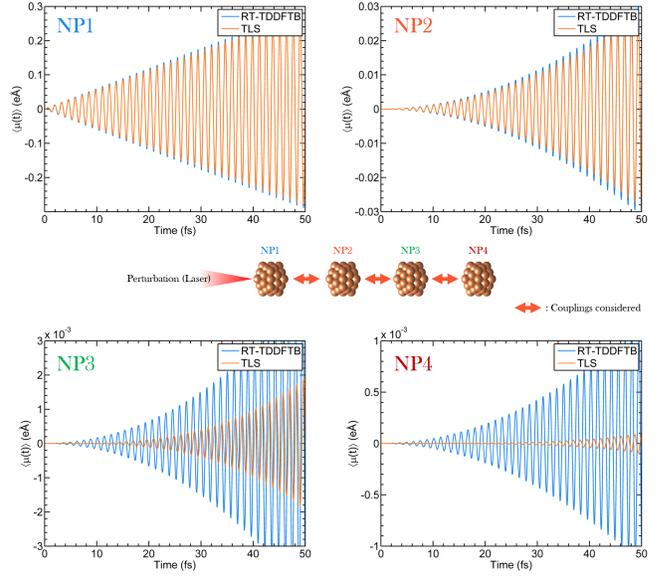


Figure 3: Comparison between the dipole moments calculated using the analytical two-level system model (TLS) that considers only the nearest-neighbor interactions and RT-TDDFTB calculations for the plasmonic nanoantenna. The dipole moments in NP3 and NP4 are severely underestimated by this analytical model.

NP1, NP2, NP3, and so on; however, we still use the dipolar approximation to describe the individual NP interactions.

3.2 Modified Two-Level System Model Including all Interactions

The primary modification in this version of the analytical model is that we now consider all of the interparticle interactions. The induced dipole moments predicted by the new analytical model closely match the RT-TDDFTB results and are summarized in Figure 4. This modified TLS model illuminates a few more significant features of the EET mechanism in plasmonic nanoantennas. Most importantly, we note that the range of electronic couplings in plasmonic nanosystems is much larger than the FRET-based cutoff limits, and restricting couplings to the conventional FRET limit severely underestimates the EET in the plasmonic nanoantenna. Furthermore, as elucidated from the analytical model, the commonly used nearest-neighbor interaction model falls short in accurately predicting EET in plasmonic nanoantennas. A more complete multi-particle interaction model, which considers interactions between all the NPs of the nanoantenna, is needed to fully characterize such a system.

4 Conclusion

In summary, we have thoroughly characterized the EET mechanism in a representative plasmonic nano-

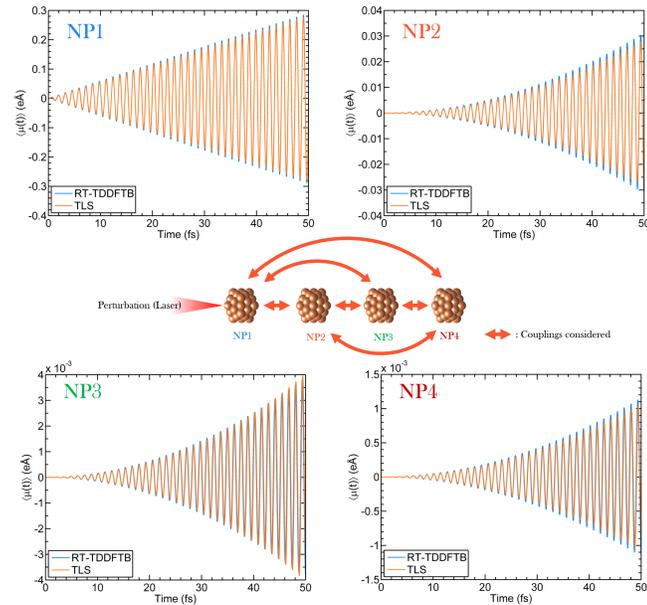


Figure 4: Comparison between the dipole moments calculated using the analytical two-level system (TLS) model, which considers interactions between all the particles and RT-TDDFTB calculations for the plasmonic nanoantenna. The multi-particle analytical model, which includes the long-range interactions, is accurately able to corroborate the RT-TDDFTB results.

antenna system using large-scale RT-TDDFTB calculations that are further rationalized by various analytical two-level model systems. Most importantly, the RT-TDDFTB simulations provide a natural approach to probe in atomistic detail the time-dependent electron dynamics in multibody plasmonic systems without recourse to customary approximations, such as nearest-neighbor, spectral overlap, or the dipole approximations to describe electronic couplings. Furthermore, we reveal highly long-range plasmonic couplings that are more than twice the conventional cutoff limit considered by FRET based approaches. We attribute this unusually higher range of electronic couplings to the coherent oscillation of conduction electrons in the plasmonic NPs. An important ramification of this long-range nature of plasmonic EET is that the “nearest-neighbor” interaction model commonly used to characterize EET is highly inadequate for plasmonic systems, even in unidirectional plasmonic antennas such as the one considered in this study. Consequently, our results provide a new viewpoint for characterizing and understanding these systems for harnessing and controlling long-range transfer of excitation energy in increasingly complex plasmonic nanosystems.

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