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Optics of plasmon- exciton nanomaterials in the strong coupling limit: self-consistent studies

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Optics of Plasmon-Exciton Nanomaterials in the Strong Coupling Limit: Self-Consistent Studies

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Our research efforts sponsored by AFOSR resulted in several collaborative works with experimental groups where the theoretical/numerical support predicted and explained experimental observations. One of our papers was chosen as the Editor's Choice Paper of the Year. We proposed and verified a simple and elegant model explaining collective exciton resonances. Our efforts on expanding Maxwell-Bloch formalism to include ro-vibrational degrees of freedom of molecules has led to predictions of narrow vibrational resonances in reflection spectra. The close collaboration with AFRL on third harmonic generation resulted in the published manuscript, where we combined for the first time plasmonics with a nonlinear dispersive macroscopic model. We thoroughly investigated implications of the strong exciton-plasmon coupling on the nonlinear photon spectroscopy and showed that such an approach can be used in nanoscale probes of hybrid systems. We wrote a comprehensive review covering all significant advances in the field of theoretical nano-optics. Overall the research program has led to 11 publications in leading peer-reviewed journals, 13 invited talks, and a set of invited lectures. We were able to accomplish almost all proposed research tasks.

Major Achievements and Breakthroughs

Following the original research plan we developed an efficient model to described *collective effects in exciton-plasmon materials*. It was successfully applied to understand experiments performed by Dr. Renaud Vallee. I am extremely proud of this work (reference #5). We were able to demonstrate that collective exciton resonances that I predicted several years ago were indeed experimentally observable. Using DOD high performance computers, we performed rigorous numerical studies of plasmonic opal arrays and their near-fields that optically drive molecular aggregates. It is only due to the fact that we had the access to DOD supercomputers the numerical part of this work was possible. In this paper we have demonstrated both experimentally and theoretically how to manipulate strong coupling between the Bragg-plasmon mode supported by an organo-metallic array and molecular excitons in the form of J-aggregates dispersed on the hybrid structure. The numerical simulations confirmed the presence of the third resonance. We attributed its physical nature to collective molecule-molecule interactions leading to a collective electromagnetic response. A simple analytical model was proposed to explain the physics of the third mode. The nonlinear dependence on molecular parameters followed from the model was confirmed in a set of rigorous numerical studies. It was shown that at the energy of the collective mode molecules oscillate completely out of phase with the incident radiation acting as an effective thin metal layer.

Proceeding further with our research plan we scrutinized optical properties of metal dimers comprised of silver nano-wires to investigate *electromagnetic energy transfer at the nanoscale* (reference #2). We considered the electromagnetic energy transport problem when wire-

to-wire distances are well below the diffraction limit. The influence of molecular excitons resonant to localized surface plasmons supported by each wire was investigated. We studied the transfer of electromagnetic energy across a subwavelength gap separating two co-axial metal nanorods. In the absence of spacer in the gap separating the rods, the system exhibited strong coupling behavior between longitudinal plasmons in the two rods. The nature and magnitude of this coupling were studied by varying various geometrical parameters. As a function of frequency, the transmission was dominated by a split longitudinal plasmon peak. The two hybrid modes were the dipole-like "bonding" mode characterized by a peak intensity in the gap and a quadrupole-like "antibonding" mode whose amplitude vanished at the gap center. When the length of one rod was varied, this mode spectrum exhibited the familiar anti-crossing behavior that depends on the coupling strength determined by the gap width. When off-resonant molecules are placed in the gap, almost no effect on the frequency dependent transmission is observed. In contrast, when the molecular system was resonant with the plasmonic line shape, the transmission was strongly modified, showing characteristics of strong exciton-plasmon coupling. Most strongly modified was the transmission near the lower frequency "bonding" plasmon mode. The presence of resonant molecules in the gap affected not only the molecule-field interaction but also the spatial distribution of the field intensity and the electromagnetic energy flux across the junction.

As a part of the research plan on *expanding our model to include ro-vibrational structure of molecules* we introduced a new efficient numerical technique based on non-Hermitian Schrödinger-type approximation of Bloch optical equations. This approximation provides a complete description of the excitation, relaxation and decoherence dynamics in both weak and strong laser fields. In this approach, it was shown that one needs only to propagate the wave function of the quantum system instead of the density matrix, providing that relaxation and dephasing are taken into account via automatically-adjusted time-dependent gain and decay rates. The developed formalism was applied to the problem of scattering and absorption of electromagnetic radiation by a thin layer comprised of interacting two-level emitters. Later on we used this model to investigate the influence of ro-vibrational degrees of freedom of molecules on optics of exciton-plasmon materials. The corresponding paper (reference #1) was chosen as *the Editor's Choice paper of the year*.

We completed work on *incorporating ro-vibrational degrees of freedom into the Maxwell-Bloch model* has led to the paper (reference #4). In this work we extended the model of exciton-plasmon materials to include a ro-vibrational structure of molecules using wave-packet propagations on electronic potential energy surfaces. The new model replaced conventional two-level emitters with more complex molecules, capable of examining the influence of alignment and vibrational dynamics on strong coupling with surface plasmon-polaritons. The model relies substantially on the paper we also published as a part of this grant - (reference #1). We have applied the model to a hybrid system comprising a thin layer of molecules placed on top of a periodic array of slits. Rigorous simulations were performed for two types of molecular systems described by vibrational bound-bound and bound-continuum electronic transitions. Calculations revealed new features in transmission, reflection, and absorption spectra, including the observation of significantly higher values of the Rabi splitting and vibrational patterns clearly seen in the corresponding spectra. We have also examined the influence of anisotropic initial conditions on optical properties of hybrid materials, demonstrating that the optical response of the system is significantly affected by an initial pre-alignment of the molecules. Our work demonstrated that pre-aligned molecules could serve as an efficient probe for the sub-diffraction characterization of the

near-field near metal interfaces. This work laid the foundation of several very intriguing applications in nonlinear nano-optics (such as influence of molecular orientation on high harmonic generation and nanoscale molecular sources of chiral fields) we intend to pursue in my next grant (currently pending).

We have investigated the implications of the strong exciton-plasmon coupling on *nonlinear photon echo spectroscopy* (reference #3). In brief, we considered the dynamics of the photon echo exhibited by exciton-plasmon nanomaterials under strong coupling conditions. Using our model based on coupled Maxwell-Bloch equations, we considered the femtosecond time dynamics of ensembles of interacting molecules optically coupled to surface plasmon-polaritons. It was shown that observed photon echo under a two-pulse pump-probe sequence is highly dependent on various material parameters such as molecular concentration and periodicity. Simulations of photon echoes in exciton-plasmon materials revealed a unique signature of the strong exciton-plasmon coupling, namely, a double-peak structure in spectra of recorded echo signals. This phenomenon was shown to be related to hybrid exciton-plasmon states. It was also demonstrated that the double-peak echo was highly sensitive to mild deviations of the coupling from resonant conditions making it a great tool for ultrafast probes.

As a part of the planned research effort on *nonlinear optics at the nanoscale* I have investigated optics of two-dimensional materials coupled to plasmon-sustaining structures (in both linear and nonlinear regimes) – (reference #8). This was done in close collaboration with Dr. Ruth Pachter (AFRL). Recently transition metal dichalcogenide monolayers (TMDs) became new building blocks in exciton-plasmon nanomaterials due to direct band-gap energetically located in the visible part of the spectrum. The latter is specifically useful when one utilizes surface plasmon-polariton states of metal nanostructures (such as periodic arrays of nano-holes, slits, etc.) to optically couple to two-dimensional materials. Moreover, such synergetic compounds present a unique opportunity to study nonlinear optical phenomena at the nanoscale owing to high third order nonlinearities exhibited by monolayers of WS_2. We have applied the numerical procedure to include material dispersion in time domain nonlinear simulations of three-dimensional systems (periodic hole arrays coupled to a monolayer of WS_2). Simulations of linear response of such hybrid systems showed expected signatures of the strong coupling. It was demonstrated that a monolayer of WS_2 placed near of periodic arrays of either slits or holes results in a Rabi splitting of the corresponding surface plasmon-polariton resonance as revealed in calculated transmission and reflection spectra. The nonlinear regime, at which the few-layer WS_2 exhibited experimentally third harmonic generation (THG), was studied in detail. TMDs do not exhibit THG because they are non-centrosymmetric, but here we used the monolayer as an approximation to a thin TMD nanostructure. We showed that in the strong coupling regime the third harmonic signal was significantly affected by plasmon-polaritons and the symmetry of hybrid exciton-plasmon modes. It was also shown that the local electromagnetic field induced by plasmons was the major contributor to the enhancement of the third harmonic signal in three dimensions. The local electromagnetic fields resulting from the third harmonic generation were greatly localized and highly sensitive to the environment, thus making it a great tool for nano-probes.

While working on *the model of fluorescence* we found that such an effect can be efficiently simulated by using semiclassical approach based on Maxwell-Bloch equations if one allows a system to interact with itself. In collaboration with Prof. Abraham Nitzan and Prof. Joseph Subotnik (both at UPenn) we found that the well-known spontaneous emission rate obtained rigorously from fully quantum description of light-matter interaction can be recovered numerically if an emitter simply interacts with itself. This approach relies on semi-empirical Abraham-Lorentz

formalism. This is highly interesting and unusual result (reference #9). The dynamics of an electronic two-level system coupled to an electromagnetic field were simulated explicitly for one- and three-dimensional systems through semiclassical propagation of the Maxwell-Bloch equations. We consider three flavors of mixed quantum-classical dynamics: (i) the classical path approximation (CPA), (ii) Ehrenfest dynamics, and (iii) symmetrical quasiclassical (SQC) dynamics. Our findings were as follows: (i) The CPA fails to recover a consistent description of spontaneous emission, (ii) a consistent "spontaneous" emission can be obtained from Ehrenfest dynamics, if one starts in an electronic superposition state, and (iii) spontaneous emission is always obtained using SQC dynamics. Using the SQC and Ehrenfest frameworks, we further calculated the dynamics following an incoming pulse, but also we found very different responses: SQC and Ehrenfest dynamics deviated sometimes strongly in the calculated rate of decay of the transient excited state.

With an emphasis on *incorporating quantum correlations into our Maxwell-Bloch integrators* I and my UPenn collaborators expanded semiclassical electrodynamics approach (reference #10). We investigated two representative semiclassical approaches for propagating resonant energy transfer between a pair of electronic systems (donor and acceptor) with the coupled Maxwell-Liouville equations. On the one hand, when the electromagnetic field is treated classically and Coulomb interactions are treated quantum-mechanically, we find that a quantum-classical mismatch leads to a violation of causality, i.e., the acceptor can be excited before the retarded EM field arrives. On the other hand, if we invoke a classical intermolecular Coulomb operator, we find that the energy transfer in the near field loses quantitative accuracy compared with Förster theory, even though causality is strictly obeyed. Thus, our work raises a fundamental paradox when choosing a semiclassical electrodynamics algorithm. Namely, which is more important: Accurate short-range interactions or long-range causality? We also applied this approach to the Raman scattering (reference #11). The dynamics of an electronic system interacting with an electromagnetic field is investigated within mixed quantum-classical theory. Beyond the classical path approximation (where we ignore all feedback from the electronic system on the photon field), we consider all electron-photon interactions explicitly according to Ehrenfest (i.e. mean-field) dynamics and a set of coupled Maxwell-Liouville equations. Because Ehrenfest dynamics cannot capture certain quantum features of the photon field correctly, we propose a new Ehrenfest+R method that can recover (by construction) spontaneous emission while also distinguishing between electromagnetic fluctuations and coherent emission.

My long-time collaboration with the experimental group of Prof. Adi Salomon has led to a series of *extensive simulations targeting understanding of optical properties of periodic arrays of nano-holes coupled to a layer of H_2TPPS_4* doped PVA. In a vast majority of current experiments on hybrid systems the J-aggregated form of the dye molecule $TPPS_4$ is used. In our work (reference #6) we consider the monomer because of its sharp absorption peak with very high absorption coefficient, features suitable for strong coupling. The basic monomer was chosen because his absorbance peak is close to the asymptote of the silver dispersion curve. The idea of this work is to place the molecular resonance as close to the asymptotic plasmon resonance of silver as possible to observe strong coupling of molecular excitons with surface plasmons at low molecular concentrations. Using my improved Maxwell-Bloch model we performed extensive simulations in three dimensions for experimental parameters. It was shown that the strong coupling regime can be achieved between the two subsystems at low molecular concentrations with negligible damping of the electromagnetic field.

We have written a comprehensive topical review on optics of exciton-plasmon nanomaterials. As many topical reviews this work was extremely challenging as it took a lot of effort to make sure that the citations are up-to-date and all pioneered papers are cited (reference #7). We decided to go beyond usual reviews and provided a set of numerical codes as a supplemental material to this manuscript such that a reader may efficiently introduce himself/herself into the field of computational nano-optics. This review provides a brief introduction to the physics of coupled exciton-plasmon systems, the theoretical description and experimental manifestation of such phenomena, followed by an account of the state-of-the-art methodology for the numerical simulations of such phenomena and supplemented by a number of FORTRAN codes. Applications to continuous wave light scattering as well as transient response and relaxation are described. Particular attention was given to so-called strong coupling limit, where the hybrid exciton-plasmon nature of the system response is strongly expressed. While traditional descriptions of such phenomena usually rely on analysis of the electromagnetic response of inhomogeneous dielectric environments that individually support plasmon and exciton excitations, here we explore also the consequences of a more detailed description of the molecular environment in terms of its quantum density matrix (applied in a mean field approximation level). Such a description makes it possible to account for characteristics that cannot be described by the dielectric response model: the effects of dephasing on the molecular response on one hand, and nonlinear response on the other. It also highlights the still missing important ingredients in the numerical approach, in particular its limitation to a classical description of the radiation field and its reliance on a mean field description of the many-body molecular system. The review also provides an outlook to the near future, where these limitations are addressed, and new novel applications of the numerical approach will be pursued.

Based on the results of the project regarding fluorescence we have initiated another work related to my proposal, namely simulations of fluorescence of molecular aggregates at plasmonic interfaces. This work is directly related to my collaboration with Dr. Renaud Vallee. His lab is in the process of developing a set of experiments, which will directly measure fluorescence lifetime and its dependencies on various material parameters. Equipped with the powerful Maxwell-Bloch/Liouville integrators developed throughout this grant we found very intriguing effect, namely spatial oscillations of fluorescence lifetime of molecular aggregates for a system comprised of either two molecular layers separated by a thin dielectric spacer or a single molecular layer near mirror. Such oscillations are due to constructive/destructive interference of electromagnetic radiation due to fluorescence. In collaboration with Prof. Abraham Nitzan I developed a very simple and elegant model to demonstrate this effect. Experimental validations are under way in the lab of Dr. Vallee. We intend to submit this work to Science as this effect has great implications in chemistry and materials sciences.

We have thoroughly investigated the numerical concepts of *lasing at the nanoscale*. Although this has not yet resulted in any publications I believe the results we have should be enough to form a basis for a good manuscript. I am currently working on it.

Partially sponsored by this grant I assembled a new computing cluster. The hardware was purchased separately at different vendors and the cluster was assembled on-site. The OS managing the machine is Rocks Cluster. The peak performance is rated at 2208 GFlops. http://www.rocksclusters.org/rocks-register/details.php?id=2179 Some results reported here were obtained solely on the new machine. Also, this cluster allowed my group to develop/debug new Maxwell-Bloch integrators based on three-dimensional domain decomposition method, which we used on DOD clusters Topaz and Thunder.

List of Publications, Presentations, and Invited Lectures resulted from this grant

Publications

1. "Non-Hermitian wave packet approximation for coupled two-level systems in weak and intense fields", R. Puthumpally-Joseph, M. Sukharev, E. Charron, *Journal of Chemical Physics* **144**, 154109 (2016). The Editor's Choice paper of the year.
2. "Plasmon transmission through excitonic subwavelength gaps", M. Sukharev, A. Nitzan, *Journal of Chemical Physics* **144**, 144703 (2016).
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4. "Molecular plasmonics: the role of ro-vibrational molecular states in exciton-plasmon materials under strong coupling conditions", M. Sukharev, E. Charron, *Physical Review B* **95**, 115406 (2017).
5. "Plasmonic opals: observation of collective molecular exciton mode beyond the strong coupling", P. Fauche, C. Gebhardt, M. Sukharev, R. A. L. Vallee, *Scientific Reports* **7**, 4107 (2017).
6. "Molecular plasmonics: strong coupling at the low concentration limit", L. Efremushkin, M. Sukharev, A. Salomon, *Journal of Physical Chemistry C* **121**, 14819 (2017).
7. "Topical Review: optics of exciton-plasmon nanomaterials", M. Sukharev, A. Nitzan, *Journal of Physics: Condensed Matter* **29**, 443003 (2017).
8. "Effects of exciton-plasmon strong coupling on third harmonic generation by two-dimensional WS_2 at periodic plasmonic interfaces", M. Sukharev, R. Pachter, *Journal of Chemical Physics* **148**, 094701 (2018).
9. "Mixed quantum-classical electrodynamics: understanding spontaneous decay and zero point energy", T. E. Li, A. Nitzan, M. Sukharev, T. Martinez, H.-T. Chen, J. E. Subotnik, *Physical Review A* **97**, 032105 (2018).
10. "Ehrenfest+R Dynamics: A Mixed Quantum-Classical Electrodynamics Simulation of Spontaneous Emission", H.-T. Chen, T. E. Li, M. Sukharev, A. Nitzan, J. E. Subotnik, arXiv:1806.04662 (2018).
11. "A Necessary Tradeoff For Semiclassical Electrodynamics: Accurate Short-Range Coulomb Interactions Versus The Enforcement of Relativistic Causality?", T. E. Li, H.-T. Chen, M. Sukharev, J. E. Subotnik, arXiv:1806.04623 (2018).

Presentations and seminars

1. "*Optics of hybrid nanomaterials: from collective exciton resonances to nonlinear spectroscopy*", invited talk, **IEEE RAPID**, August 22-24, 2018.
2. "*Optics of exciton-plasmon nanomaterials beyond the strong coupling*", invited talk, **TSRC Conference, Plasmon-Exciton Coupling**, Telluride, Colorado, June 16, 2018.
3. "*Optical properties of exciton-plasmon nanomaterials: from collective exciton resonances to nonlinear spectroscopy*", invited colloquium, **Center for Nanoscale Materials, Argonne National Laboratory**, September 6, 2017.

4. "*The quest of strongly coupled nanomaterials: from collective exciton resonances to nonlinear spectroscopy*", invited seminar, **Center de Recherche Paul Pascal, CNRS**, Pessac, France, July 6, 2017.
5. "*The quest of strongly coupled nanomaterials: from collective exciton resonances to nonlinear spectroscopy*", invited seminar, invited seminar, **Laboratory of Charles Fabry, Institute d'Optique**, France, June 22, 2017.
6. "Modeling aspects of *molecular plasmonics*", invited seminar, **Department of Chemistry, University of California at San Diego**, December 13, 2016.
7. "*Molecular plasmonics: optics of molecular aggregates at plasmonic interfaces*", invited seminar, **Department of Chemistry, University of California at Los Angeles**, October 11, 2016.
8. "*Molecular plasmonics*", **Special seminar, Institute of Nanotechnology, Bar-Ilan University**, Rama-Gan, Israel, July 31, 2016.
9. "*Modeling aspects of optical phenomena in exciton-plasmon materials*", **Physics Colloquium, Department of Physics, Lehigh University**, Bethlehem, April 27, 2016.
10. "*Modeling aspects of optical phenomena in exciton-plasmon materials*", **Physical Chemistry Seminar, Department of Chemistry, University of Pennsylvania**, Philadelphia, April 21, 2016.
11. "*Optical functionality of plasmon-exciton nanomaterials in the strong coupling regime*", invited talk, **APS meeting**, Baltimore, March 14, 2016.
12. "*Optical phenomena at plasmonic interfaces*", invited seminar, **Center de Recherche Paul Pascal, CNRS**, Pessac, France, February 19, 2016.
13. "*Optical phenomena at plasmonic interfaces*", invited seminar, **ISMO, University Paris-SUD**, Orsay, France, February 17, 2016.

Invited lectures

I gave a set of three lectures on computational nano-optics this summer at Center de Recherche Paul Pascal, CNRS, Pessac, France. This set of three lectures is designed to give students a flavor of computational nano-optics; it starts with motivations, general ideas and gradually proceeds to modern numerical techniques such as FDTD and parallel simulations along with coupling of Maxwell's equations to quantum dynamics.

Lecture I: "*Fundamentals of plasmonic materials - why do we need this and why should we care?!*": This hour long lecture introduces general concepts of nano-optics and plasmonics with many modern examples of plasmonic systems. We discuss major ideas in nano-optics and proceed to talk about evanescent waves and plasmon- polaritons. The lecture sets the stage for next lectures on computational aspects of plasmonics.

Lecture II: "*Simulating optics of plasmonic nanomaterials: shut up and calculate!*": This lecture discusses ideas behind a widely used numerical technique called finite- difference time-domain (FDTD) which is frequently utilized to numerically integrate Maxwell's equations. The general concepts of FDTD are introduced and discussed with regards to computational plasmonics. The concept of parallel simulations is also discussed.

Lecture III: "*Optics of hybrid nano-materials: well, how about some quantum mechanics?*": In this final lecture we discuss currently developing research field of hybrid nanomaterials - sys-

tems comprised of plasmonic structures fairly well discussed in previous lectures and quantum emitters (quantum dots, molecular aggregates, dyes, etc.). We outline numerical techniques needed to couple Maxwell's equations with quantum dynamics and follow several examples considering strong coupling of molecular excitons and plasmon-polaritons.

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Archival Publications:

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