Proposal

Computational Nanophotonics: Modeling Optical Interactions and Transport in Tailored Nanosystem Architectures

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Theory, Modeling and Simulation in Nanoscience

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TABLE OF CONTENTS

Abstract Page 4
Narrative
I. *Background and Significance* 5
II. *Preliminary Studies* 7
III. *Research Design and Methods* 10

A. Scientific Problems and Theoretical Methods for Metal Nanoparticle and Hybrid Nanophotonics Systems, and their Assemblies 10

A.1. Electrodynamics 10
A.2. Structural, Electronic, and Optical Properties 13

B. Applied Mathematics and Software Development 18

C. Summary: Anticipated Major Research Progress 20

IV. *Literature Cited* 22
V. *Budget and Budget Explanation*
VI. *Other Support of Investigators*
VII. *Biographical Sketches*
VIII. *Description of Facilities and Resources*

ABSTRACT

We propose (i) To carry out realistic theory, modeling, and simulations of light interacting with tailored architectures of metal nanoparticles and hybrid systems that also include, e.g., quantum dots and molecular wires, and (ii) To develop a comprehensive suite of high performance, parallel simulation tools, NSTOP (Nanoscale Structure, Transport, and Optical Properties), for such purposes that will be made generally available. Regarding (i) : Our nanophotonics simulations will allow us to learn how to control light on the nanoscale, e.g. to replace electrons as information carriers in optical or opto-electronic devices, or to create novel chemical and biological sensors. An important emphasis of our work is carrying out detailed electronic structure and molecular dynamics studies to learn about structural, electronic, and optical properties of the metal nanostructures, i.e., obtaining more microscopically correct information that will, ideally, be employed in our continuum-level simulations of light interacting with the nanostructures. Regarding (ii): NSTOP will contain state-of-the art tools for the computation of structural and electronic/optical properties of nanosystems and time-domain and frequency-domain simulations tools for light interacting with nanosystems. These tools will be scalable, extensible, portable and therefore suitable for a broad range of users and computer platforms. Common Component Architecture (CCA) will be the software engineering construct that will integrate the different components of NSTOP. Parts (i) and (ii) are entwined: it is only possible to develop genuinely useful codes for the community in the presence of

sophisticated applications work because of the complexity of the underlying scientific problems. There are many critical applied mathematics and computer science issues to be addressed in developing a genuinely useful, accurate and efficient set of such tools, including the incorporation of novel meshes and pseudospectral approaches into the simulations codes and the development of robust techniques that simultaneously couple the classical, continuum level electric and magnetic fields to nanoscale quantum objects (e.g., quantum dots and molecular wires).

I. BACKGROUND AND SIGNIFICANCE

Recent advances in nanofrabication technology have produced exciting opportunities for using ordered structures of metal, semiconductor and other nanoparticles as nanophotonic devices for the control and manipulation of electromagnetic signals for a variety of purposes [1-12]. For example, the interaction of light with noble metal nanoparticles undergoing aggregation has recently proven to be of significant importance in the development of chemical and biological sensors [2-4]. There are *immense* opportunities for theory, modeling and simulation in nanophotonics. Experiments have only just begun to scratch at the surface of the nanophotonic properties of various nanoscale architectures, and we are just beginning to learn how to assemble the relevant architectures. The "Killer App" of nanophotonics, in our view, is yet to be found. Theory and simulation are needed not only to complement existing experiments, but to lead the way through a very dense forest of scientific possibilities and to suggest new possibilities. The present proposal pulls together a "critical mass" of theoretical/computational scientists, applied mathematicians, and computer scientists that will be able to both carry out cutting-edge nanophotonics simulations *and* develop a comprehensive suite of community codes for nanophotonics. We now discuss in greater detail a few of the exciting nanophotonics problems that we are interested in.

The science behind chemical and biological sensors [2-4] noted above involves not only the chemical properties of silver and gold (which can easily bind organic molecules), but the extremely intense optical transitions associated with surface plasmon (SP) polaritons [13-15] in the nanoparticles, i.e. resonant interactions between the electronic charge density near the surface of the nanoparticles and the applied electromagnetic field. Nanoscale optical fields excited by external radiation close to metallic nanoparticles are greatly enhanced due to such SP polaritons [15 - 18]. Due to these “hot spots”, optical responses are strongly enhanced and can be large enough to allow, in particular, observation of Raman scattering from a single molecule attached to a metal colloidal particle [19, 20]. A promising related area is local optical nanosize probing by a metal tip that creates enhanced optical fields in its vicinity. This was demonstrated for near-field fluorescence microscopy based on two-photon excitation [21], local field enhanced Raman scattering [22] and second harmonic generation [23]. Such local fields could be used for linear and nonlinear optical nanoprobing and nanomodification [24].

In addition to the use of nanoparticle arrays in chemical and biological sensing and related applications, there is significant interest in using them for controlling the propagation of light with submicron resolution, which could lead to new classes of opto-electronic devices. Recent work by Ebbesen and co-workers [5-7] dramatically demonstrates how specially designed aperture structures composed of lines or arrays of nanoparticles that are capable of undergoing SP excitation can dramatically influence the transmission of light through subwavelength holes and slits. There has also been interest in using nanoparticle chains to alter the direction of propagating electromagnetic waves and to create SP-based optical devices [8-12]. For example, Atwater and co-workers have studied the use of chains of nanoparticles to propagate and control plasmon excitation [9-11], and Krenn and co-workers demonstrated non-diffraction-limited light transport by gold nanowires [12].

Assemblies of metal nanoparticles and semiconductor quantum dots (QDs) and, more generally, metal/semiconductor nanocomposites, are of great interest owing to their reach and useful properties [25-27]. These are due to the combination of giant-enhanced local fields created by metal nanoparticles and tunable electronic properties of semiconductor nanoparticles. In particular, spectra of QDs are tunable by

their chemical composition, doping, and sizes. Nanocrystal QDs are used as fluorescent biological labels [25] and as two-level emitters in the active medium of semiconductor lasers [26]. Another area of metal/semiconductor nanooptics of especially fundamental and applied interest is that of ultrafast phenomena on the nanoscale. Experimentally, it is a very challenging field. Nevertheless, significant progress has been reported recently in measuring ultrafast responses of nanoparticles [28, 29]. We have found that the spatial distribution of ultrafast optical excitation in materials on the nanometer spatial scale and femtosecond temporal scale can be coherently controlled by the phase of the excitation ultrashort pulse [30]. In future nanochips, the semiconductor QDs will likely perform computational operations (classical or quantum), while metallic components will play the role of nanoantennas, supplying energy and synchronizing computations. Such applications will require ultrafast processes.

One potentially important electronic device application would involve the coupling of SP excitation to electrical current that would be transported to and from the nanoparticles that are linked by molecular wires. In this application we envision that the nanoparticles would replace micron scale electrodes that are currently used in molecular wire circuits, in which case SP excitation would influence transport of electrons at the molecular junctions. For theoretical discussions of molecular wire junctions, see Refs. [31, 32]. The coupling of external radiation into the molecular transport junction is a difficult problem in electrodynamics and the role of SP interactions has not yet been addressed in molecular wire studies.

So far our discussion has been focused on the electrodynamics and quantum dynamics of nanophotonics devices. Now we consider the fundamental structural and electronic properties of metal clusters/nanoparticles and their assembly into various nanoscale architectures. These properties, which depend on the elemental composition, and include size, shape and geometric structure, are ultimately responsible for the photonic behavior. The size, shape and structure depend on the conditions and the environment under which the particles nucleate and grow. Atomic assembly into clusters/nanoparticles may take place in the gas phase, on substrates, and in solutions. Understanding the fundamental mechanisms that underlie the nucleation and growth processes and the key variables and parameters they depend on is crucial for controlled growth of particles with desired characteristics. The same is true for nanoarchitectures assembled from either atoms or clusters/nanoparticles used as “superatom” building blocks. An important part of our project will be to develop a clearer scientific understanding of the central problems of the assembly of nanoscale architectures and also to learn how to predict the optical response (e.g., effective dielectric constants or even non-local dielectric constant behavior) that might be different from bulk material expectations. This understanding will be translated into additional computer software associated with molecular dynamics (MD), structure optimization, and ab initio based optical properties, for example, that will be added to our suite of nanophotonics codes.

This proposal will use theory and computation to study the basic science of potential nanophotonics systems such as those described above, with emphasis on the assembly, optical and electronic transport properties of arrays of metal nanoparticles and metal/semiconductor hybrid systems. Notice that this work spans a range of physical scales, ranging from the most microscopic level (insofar as nanophotonics is concerned) of electronic structure to continuum level electrodynamics. An essential aspect of our proposed work is that it will directly lead to the needed applied mathematics, numerical methods and software for the realistic modeling of such problems, which will be shared freely with the research community. A large suite of simulation tools, termed NSTOP (Nanoscale Structure, Transport, and Optical Properties) will be developed that will provide "one-stop" shopping for other researchers in nanophotonics.

We have put together a team of scientists, applied mathematicians and computer scientists that are *ideally-positioned* to carry out the proposed work. Gray (CHM, ANL) and Schatz (NWU) have expertise in time-domain and frequency-domain computational electrodynamics of metal nanoparticles, and the related area of quantum dynamics. Ratner (NWU) and Stockman (GSU) are experts in the realm of theory and modeling of hybrid systems including molecular wires and quantum dots. Jellinek (ANL) is an expert in the molecular dynamics, structure, and electronic properties of metal clusters and nanoparticles. Jackson (CMS) and Ogut (UIC) are experts in optical response properties based on high level ab initio electronic structure. Finally, Argonne's Mathematics and Computer Science Co-PIs are fully equipped to discover and implement the key applied mathematics and high-performance computing components, including pseudospectral methods for partial differential equations (Fischer), high-performance parallel numericall methods (Smith), component interface definition, automatic differentiation, and performance analysis and optimization (Norris). In addition to the close physical proximity of most of the PIs, the project will also benefit from the presence of several experimental leaders in photonics and related matters in the Chicago area (Scherer, Van Duyne, Mirkin, Wiedderrecht and the experimental component of the Argonne Cluster Studies group).

II. PRELIMINARY STUDIES

The assembled team of PIs has already carried out a variety of theoretical studies pertaining to nanoscience and, in particular, nanophotonics demonstrating both our ability to carry out the proposed work and the soundness of the proposed scientific and computational ideas.

Schatz is a recognized expert in modeling the photonic properties metal nanoparticles. Recently, for example, Schatz, Van Duyne and coworkers [33] have studied the electromagnetic interactions between noble metal nanoparticle arrays, pictured in Fig. 1, by measuring the extinction spectra of two-dimensional arrays of Au and Ag cylinders and trigonal prisms that were fabricated with electron beam lithography. The particles in these arrays were quite large (200 nm diameter) and the spacings were varied from 230 to 500 nm. The extinction spectra typically have a SP polariton maximum in the 700-800 nm region of the spectrum, and this maximum blue shifts as lattice spacing is reduced (the opposite behavior to what has been seen in the past for smaller particles that are more closely spaced), with typically a 40 nm decrease in λ_{max} for a 100 nm decrease in lattice spacing. The extinction spectra were modeled using the discrete dipole approximation (DDA) and co and T-matrix

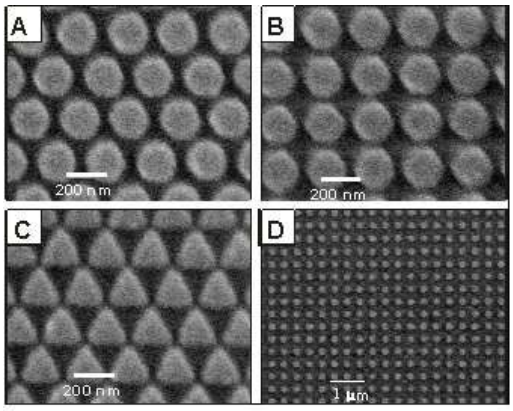

Figure 1. Scanning electron micrographs of metal nanoparticle (MNP) arrays (all 35 nm in height). (A) Cylindrical MNPs with a diameter of 200 nm in hexagonal arrangement. (B) Cylindrical MNPs with a diameter of 200 nm in square arrangement. (C) Trigonal prism MNPs with a perpendicular bisector of 170 nm in hexagonal arrangement. (D) Larger

theory, and the observed spectral variations are in good qualitative agreement with experimental data. Moreover, the computational analysis indicates that the blue shifts are due to radiative dipolar coupling between the nanoparticles and retardation effects. This suggests that spectral changes resulting from particle interactions can be used either as a sensing mechanism and as an optical switch.

In addition to isolated particles and periodic arrays, it is also of interest to consider non-periodic configurations. Gray is well known for developing methods for solving the time-dependent Schrödigner wave equation, and applying these methods to computationally challenging problems. Much of this expertise can be translated into solving Maxwell's wave equations and Gray has established a new research program in time-domain electromagnetics of metal nanoparticles. Recently, Gray and Kupka [34] investigated the electrodynamics of arrays of silver nanowires with the Finite-Difference Time-Domain (FDTD) [35] method. The empirical, frequency-dependent dielectric constant of the metal, which can have an imaginary part and a negative real part, was described with a Drude model fit to the specific frequency-range of interest. (The auxiliary differential equations method of Ref. [35] leads to a stable numerical propagation of the time-domain equations and can be extended to much more general dielectric behavior.) They also showed how to obtain good quality scattering and absorption cross sections with the FDTD method even in the presence of strong SP polariton resonances. Various linear arrays were investigated in the hope of finding nanoscale localization and propagation of radiation. It was suggested that somewhat more structured arrays, such as the "optical funnel" configuration displayed in Figure 2, might prove useful for such purposes. (Partial motivation for this configuration was provided by the work of Stockman and co-workers [36] to be discussed in the next paragraph.) In collaboration with co-PI Smith (MCS), using the PETSc library of mathematical kernels (www.mcs.anl.gov/petsc). This code is not yet robust but initial results run at the National Energy Research Supercomputer Center (NERSC) are encouraging. For approximately the same grid size used in Fig. 2, parallelization over 64 processors was within 10% of ideal and rolled off to approximately 50% by 256 processors.. This kind of dramatic expansion of capabilities is essential to study much larger and/or more complicated nanowire arrays than those depicted in Fig. 2. We have also begun to explore more general sorts of situations such as dielectrically coated nanowires and metallically-coated dielectrics [37].

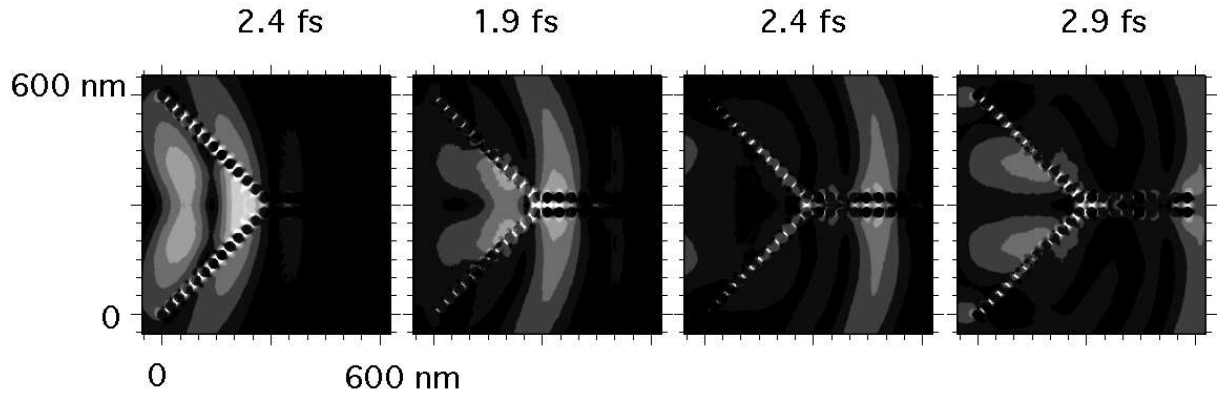

Figure 2. Depiction of how a optical pulse (vertically polarized and moving from left to right) interacts with 30 nm diameter silver cylinders (cylindrical axis out of the page) configured to form a funnel-like structure. A linear scale with white representing the most intense electromagnetic field magnitudes and black representing no field is used. Analysis of the energy flux at the mouth of the tube indicates 100 nm scale localization.

Stockman and Ratner are recognized experts in developing theories and models of somewhat more complex nanoscale phenomena and we outline some of their relevant recent results. Recently, for

example, Stockman and co-workers developed an effective and highly stable computational method based on spectral expansion of Green's functions [30, 36]. They used this method to study the coherent control of spatial localization of optical fields on the nanoscale. (See Refs. [38] and [39] for more general discussions of coherent control.) In particular, they showed how to localize energy at the tip (apex) of a V-shaped silver nanostructure [30]. More recently, Stockman and co-workers have proposed how to achieve surface plasmon amplification by stimulated emission of radiation (spaser) [27], where the resonator is a silver nanoparticle and the active medium is a nanometer-thin layer of QDs. The spaser radiation consists of surface plasmons that are bosons and undergo stimulated emission, but in contrast to photons can be localized on the nanoscale. The emitters (QDs) transfer their excitation energy by radiationless transitions to a resonant nanoparticle that plays the role of a laser cavity. These transitions are stimulated by the SPs already in the nanosystem, causing buildup of a macroscopic number of SPs in a single mode. A spaser generating a dark SP mode provides a unique possibility for a background-free nano-spectroscopy, where the spaser by itself does not radiate in the far zone. However, molecules in the spaser vicinity are strongly excited by the SP local fields, and their radiation is further enhanced by the metal nanoparticles (similar to SERS) and can be detected in the far field. Ratner has made fundamental contributions to the theory of molecular electronics. His recent work on molecular wire junctions [32] has shown how to tune conductance via physical or chemical alteration of molecular wires, which provides motivation for some of our proposed work below.

Jellinek is a recognized expert in theoretical and computational studies of small metallic systems. Over more than a decade and a half he and coworkers are involved in cutting edge explorations of a broad variety of structural [40-45], thermal [40,41,46-51], electronic [45,52-54], and chemical [55-57] properties of one- and two-component (alloy) metal clusters. These studies use a hierarchy of theoretical/computational approaches and tools, which include first-principles-based Molecular Dynamics (MD) [58] and Monte Carlo (MC) [59] techniques, high-level density functional theory (DFT) [43, 52-54], semiempirical modelling of metallic cohesion and its use in large-scale MD simulations [40-42, 44, 46-51, 55-57, 60], etc. Jellinek's group also developed and applied new theoretical/computational concepts and methodologies. Among these area new, superior to least-squares, fitting procedure [60]; novel dynamical and thermodynamical analyses specifically tailored for finite systems [51]; a new scheme for computation of the electron binding energies within DFT [61]; and others. These were used to study the evolution of properties of atomic clusters of different metals with their size. The most recent example is the size-induced nonmetal-to-metal transition. It turns out that small clusters of elements that are metals in bulk quantities may not possess metallic attributes. These attributes then emerge as the clusters grow in size. Recently we applied our new scheme for computation of electron binding energies within DFT to study the size-induced transition to metallicity in magnesium clusters [45, 53, 54]. Not only are our computed results in quantitative agreement with the recently measured experimental data [62], but they unravel the true meaning of these data. Of special relevance to this proposal is Jellinek and co-worker's study of an aluminum clustert/nanowire contact between two aluminum plates [63]. The study explores both the structural and electronic (conductivity) properties of the nanowire; the analysis of conductivity uses the Landauer [31, 32] approach.

Jackson and Ogut's previous work of relevance concerns ab initio based electronic structure and optical properties of metallic clusters and materials. Jackson's experience ranges from the development of highly accurate Gaussian-orbital-based DFT methods [64-66] to using these methods to study the structural and electronic properties of atomic clusters, including cluster polarizabilities.[67, 68] Also of relevance to the present proposal has been the development of new search algorithms for finding the structural global

minima of intermediate-sized clusters.[69, 70] This work has produced DFT global minima for Fe clusters containing up to 26 atoms [70] and the first DFT-based structural models detailing the well-known shape transition in Si clusters.[69, 71] A second recent focus has been on issues related to magnetic ordering in Fe and Mn clusters.[72, 73] Ogut has extensive experience in first principles modeling of materials, in particular clusters and nanocrystals. Over the last seven years, he has performed ab initio pseudopotential total energy calculations and molecular dynamics simulations for atomic, electronic, and optical properties of various semiconductor and metallic clusters and nanocrystals [74-81]. He played an important role in the development and implementation of a large scale real-space finite-difference pseudopotential electronic structure code [82], and performed the first ab initio calculation on a Si-H nanocrystal with more than 1000 atoms, as well as time-dependent density-functional calculations on systems with more than 250 atoms. His recent work on screening in quantum dots allowed efficient real-space calculations of very large dielectric matrices of confined systems from first principles [83].

Smith has extensive expertise in the development of high-performance numerical algorithms for the solution of PDEs, leading to software and computer science results of central relevance to our proposal. He is one of the principal developers of the Portable, Extensible Toolkit for Scientific Computations (PETSc) [84, 85], a suite of data structures and scalable parallel algorithms for the solution of scientific applications modeled by partial differential equations. PETSc comprises a hierarchy of libraries ranging from low-level distributed data structures for meshes, vectors, and matrices to high-level linear, nonlinear, and time-stepping solvers. High-level abstract interfaces hide data representation details and parallel execution specifics, promoting ease of application development and code reuse. As noted earlier, Smith has contributed to the development of a parallelization of the basic FDTD code using the PETSc framework, resulting in significant performance improvements and allowing the solution of much larger problems.
Fischer, known for his multidomain spectral work [86-89], will bring extensive applied mathematics expertise in the construction of optimal algorithms for the NSTOP suite.
Norris is an active member of the Common Component Architecture forum (http://www.cca-forum.org), a working group whose objective is to define a minimal set of standard interfaces for the development of scientific components. In addition, she has developed interfaces and components for the numerical solution of PDEs and optimization [90]. Some of this work that was recently recognized in DOE's top 10 science achievements in 2002 (http://www.sc.doe.gov/sub/accomplishments/top_10.htm). Her expertise in component software design and development will facilitate the development of the NSTOP suite, ensuring ease of use, portable high performance, and composability. Especially relevant to this proposal is Norris's experience with the development of interoperable multi-language numerical components using the Scientific Interface Definition Language (SIDL). Norris is also involved in the development of tools for automatic differentiation (AD) [91, 92]. AD support has recently been integrated into PETSc, providing accurate and efficient derivative computations used in the solution of PDEs.

III. RESEARCH DESIGN AND METHODS

The main goals of our proposed work are :

- To learn how to manipulate light on the nanoscale in tailored architectures to achieve desired outcomes, e.g. to replace or supplement electrons as information carriers for all-optical or optoelectronic devices, or to create novel nanoscale chemical and biological sensors based on the optical or electronic response of nanoparticle assemblies, or to control current flow in molecular

transport junctions.

- To develop a comprehensive suite of high performance nanophotonics codes, capable of realistic time and frequency domain simulations and complex material (e.g., metal, semiconductor) modeling, as well as suites of codes for determining the assembly and material properties of nanoscale architectures: NSTOP (Nanoscale Structure, Transport and Optical Properties)

The *ideal* achievement of the first goal above will involve a feedback over scales:

(i) Continuum level simulations of light interacting with nanoparticle architectures, including studies of plasmon excitation and propagation as a function of nanoparticle arrangement, composition, excitation source, local dielectric environment, electrical control, and the presence of additional components such as near field sources, photonic cavities, diode emitters, and nonlinear optical components.

(ii) Electronic structure, molecular dynamics and related studies to obtain structural and optical properties of metal and semiconductor nanostructures, including the frequency-dependent material properties needed for electrodynamics and transport modeling. This information will feed into (i).

We will of strive towards the above ideal whenever possible, e.g. especially in the case of small metal nanoclusters. Some of the more complex and larger nanosystems we have in mind cannot yet be accurately analyzed at level (ii) above. In those cases we will either use smaller cluster information to guide us or empirically model the relevant dielectric behavior.

A. Scientific Problems and Theoretical Methods in the Computational Nanophotonics of Metal Nanoparticle and Hybrid Systems, and their Assemblies

A.1 Electrodynamics

Systems of interest. We should emphasize that since the field of nanophotonics is a relatively new field, there are many types of scientific studies that could be of relevance to opto-electronic devices and sensing. We are therefore interested in investigating a range of systems, including light interacting with purely metallic systems, mixed metal/semiconductor systems and metal/electronic conductor systems. Note this represents a logical progression of increasing theoretical and computational complexity. The electrodynamics calculations naturally require structural, electronic and optical information about the underlying components of the nanoarchitectures. See the next subsection, A.2, for more detailed considerations of these latter elements.

We will first investigate arrays of noble metal (e.g., Au and Ag) nanoparticles, considering how size, shape and array configuration alter the basic properties of light propagating through such systems. Basic scientific issues include how and why surface plasmon resonances are altered and whether or not nontrivial nanoscale localization and propagation of electromagnetic energy occurs. We will also study such arrays embedded in different dielectric materials or placed on top of a dielectric material such as silicon. The

initial portions of this work will focus on the metallic nanowires discussed in the Preliminary Results, Sec. II, but we will quickly extend this work to genuinely three-dimensional nanoparticles such as spheres, ellipsoids and more complex shapes.

While there is clearly much to do with systems composed of noble metal nanoparticles, certain compound or hybrid systems are also of great interest as potential nanophotonics systems. For example, recent theoretical and experimental work has suggested that coatings can be used to fine-tune single nanoparticle surface plasmon optical properties [93] and our preliminary results (Sec. II) have also demonstrated that coatings can significantly affect arrays of nanoparticles. See especially the work of Hallas and co-workers, pointing to how SP resonances can be controlled in metal/dielectric nanoshells [94]. We therefore plan to examine how a dielectric coating around the metal nanoparticles will alter the optical properties of more general and complicated arrays. The converse case, i.e., a dielectric core and metallic shell, will also be considered.

Another more complex situation of direct relevance to emerging experimental efforts is the electrodynamics of the metal nanoparticle systems discussed so far but also in the presence of a near-field probe such as an atomic force microscope tip [22,23,95]. The nature of the specific shape of the tip and the role of imperfections can readily be modeled with, for example the FDTD and GF codes we will develop (see theoretical methods below) and is a matter of great experimental interest.

The electrodynamics of hybrid systems such as metal nanoparticle arrays with semiconductor quantum dots embedded can also be studied with our approaches (see Theoretical Methods below). Semiconductor quantum dots have very high fluorescence efficiencies and thus could be excellent near-field sources for optoelectronic devices. Quantum dots (QDs) can also be used for as photodetectors, and quantum dots can be chemically functionalized in a variety of ways that makes it relatively straightforward to position a dot at specified locations on a lattice of metallic structures. While surface plasmon generation by stimulated emission of radiation (spaser) was proposed earlier [27], we would like to consider lasing in the visible or near-infrared regions from a nanocomposite containing metallic nanoparticle and semiconductor QDs. In such a laser, the active medium is constituted of QDs, and the resonator is the metallic composite. The QDs can be population-inverted and then their resonant transition can drive the SP polaritons in the metallic component that couple to out-going light waves. Note SP polariton lasers are known [96], but they work only in the infrared. The proposed metal-QD composite will be most efficient at ≈ 1 μm in the practically interesting communications range.

In the molecular wire transport calculations area, use of the generalized Landauer approach has proven useful in the calculation of actual current/voltage characteristics for coherent transport through molecular wire junctions [97, 98]. When an electromagnetic field (photon coupling) process is added, we are aware of a few investigations of the expected response. Recent work of Coalson and co-workers [99] has used the Floquet representation to construct pseudo states corresponding to photon dressing of the molecular eigenstates, while Atabek and co-workers [100] have utilized a more straightforward perturbation theory analysis. In both cases, however, the authors have assumed that the photon field couples by the usual semiclassical linear $\mu \cdot \mathbf{E}(t)$ structure. This is almost certainly inaccurate for any realistic molecular junction, because an electromagnetic wave will not propagate as a simple plane wave. Full analysis of how excitation and quenching in such structures would occur could be very important in predicting the effects of photoexcitation in molecular transport junctions. We will pursue such an analysis both formally and numerically, based on our progress in both nanoparticle optics and in nanoparticle/molecule coupling. A

particularly challenging hybrid system is the metal/molecular/metal transport junction, because of the inhomogeneities expected in the electromagnetic scattering problem. Typical organic molecules have relative dielectric constants of the order of ε_R 2, and calculating the excitation and quenching process when such molecules are illuminated while bound to metallic electrodes is also a challenging and significant issue.

Theoretical methods. What we see from this discussion of past work in Secs. I and II is that classical electrodynamics provides a useful tool for modeling the transmission and shaping of photons by metallic (and other) nanostructures. Applications of these methods usually assume that one can model the polarization response using a local dielectric function. For many of the relatively large nanoparticles generally of interest to us in this study this should be a good approximation, and furthermore it is possible to incorporate non-local effects if needed. [101]. The electronic structure work to be outlined in Sec. IIIB will also address size and shape dependencies that may arise on the nanoscale, as well as some non-local aspects in some cases.

We propose using classical electrodynamics to study the interaction of light with metal structures. All the methods mentioned so far (FDTD, DDA, T-matrix and Green's function) are already available for this purpose, but it is possible to make significant improvements in them that we hope will extend their capabilities to treat the larger structures of interest in nanophotonics. Here is what we plan to do.

1. *Finite-Difference-Time-Domain (FDTD):* This is an explicit numerical solution of the relevant time-dependent Maxwell's equations employing spatial grids and simple finite differencing ideas [35]. Fourier transformation techniques can be used to provide information about a wide range of wavelengths from a single FDTD propagation. Simply inspecting the time-evolution of the fields can also provide useful mechanistic insights. The calculations we have done so far have assumed z-invariance (cylindrical symmetry) but three-dimensional generalization of our codes is straightforward in principle. More accurate ways of modeling complex, frequency-dependent dielectric properties (e.g., metals) will also be developed, e.g. by the inclusion of not only Drude but additional Lorentzian contributions to the dielectric constant within the context of the auxiliary differential equations approach of Ref. [35]. Accurate 3D modeling will be expedited by a variety of improvements, including more sophisticated meshing and derivative approximations, and parallelization.

2. *Discrete-Dipole-Approximation (DDA):* This is a finite element based approach in which each element is assumed to be a polarizable object with a polarizability that is determined by the dielectric constant of the material that is being represented [102, 103]. This method has so far been implemented in a fixed frequency (time independent) mode with the assumption that the only applied field is a far-field plane wave. However this restriction can be relaxed, such that one also considers near-field excitation, and furthermore it is possible to rework DDA into an explicitly time-dependent theory. In addition, we would like to take advantage of recent work by Martin and co-workers [104] who have developed methods for describing interacting dipoles in the presence of an infinite substrate.

3. *T-matrix:* In this time independent approach [105], one expands the solutions associated with each particle in vector spherical harmonics, and then the expansion coefficients are determined by imposing electromagnetic boundary conditions on the superposition of expansions from all the particles at the particle surfaces. This method has the advantage that it provides a more efficient treatment of each particle than either FDTD or DDA, and as a result it can be used for upwards of 1000 particles. However the

currently developed versions of this approach have been confined to spherical particles, with no substrate, fixed frequency and only plane wave illumination, so many of the same limitations that apply to DDA also apply to this approach. Obviously we would like to circumvent these limitations, but unlike the DDA approach which is easily adapted, the T-matrix method will require significantly more analytical development. In the proposed research we would like to tackle the treatment of near-field illumination, as this can be done for spherical particles within the framework of the existing theory. Also, we plan to solve the spherical particle limitation by using a multipole representation of the DDA solution for each particle with the coupled T-matrix equations. This will require reworking DDA so that the applied field is now a spherical wave rather than a plane wave, however this is closely related to what we will do in our DDA work described above.

4. *Green's Function (GF) method* : previously discussed [30,36] GF method developed for quasistatic approximation to electrodynamics problems will also be further developed and applied. This method is based on the spectral expansion of the retarded GF of the system over a set of the eigenmodes that are surface plasmon excitations of the system. These surface plasmon modes are found on a grid by solving the corresponding quasi-electrostatic equations. This method has a significant advantage of being exceptionally stable, because many exact properties of the Green's function, including causality and analyticity, are exactly preserved by the form of the spectral expansion, irrespectively of the precision with which the surface plasmons are found numerically. Then we will use this basis, instead of, e.g., spherical harmonics to solve the electrodynamic problems. We expect that both technical complexity and CPU and memory requirements for this method will be similar to the T-matrix method.

Each of the above-mentioned methods (FDTD, DDA, T-matrix and GF) has its own advantages and areas for efficient applications. E.g., the FDTD method can be used to follow the time-evolution of arbitrary pulses of light interacting with nanosystems, whereas the other methods can more naturally describe frequency-resolved scattering states. The FDTD method also can be applied to very arbitrary nanostructures but its computational effort, being based on simple grids of three-dimensional space, may not be as good as that associated with the three frequency-resolved techniques above. The DDA is efficient for spatially well-isolated nanoparticles of smooth shapes. The T-matrix method can treat higher multipole components, but its numerical efficiency in the nanoscale needs to be investigated. The GF method is stable and has excellent nanoscale resolution, but it is not highly memory efficient and needs to be developed for coupling to waves on the micro- to macro-scale. Of course, part of our work will to be to learn which method is most appropriate for a given situation.

One advantage is that we not only can choose out of this arsenal of methods for a specific problem, but develop hybrid methods incorporating advantages of each individual method. For example, we plan to develop a new method that will use FDTD to find fields with a 0.1 μm resolution, then use these fields as boundary conditions for the GF method that will define 1 nm resolution fields and propagate them in time by 0.1 fs time steps. The fields found in such a way can be used as initial conditions for the next FDTD iteration.

A.2 Structural, Electronic, and Optical Properties

The central scientific issues here are the structural, electronic, and optical (response) properties of metal cluster/nanoparticle systems as a function of the elemental composition and size, and of the different architectures assembled from these clusters/nanoparticles.

Structural and electronic properties. We will use state-of-the-art nonlocal DFT to explore the structural and electronic properties of the particles. An important part of the studies will be validation of the choice of the exchange-correlation functional(s) and basis set(s). Available high-level quantum chemical and experimental data will be used as a basis for validation. Both all-electron (for clusters with tens of atoms) and pseudopotential (for clusters and nanoparticles with hundreds of atoms) treatments will be performed. The computations with pseudopotentials (the only feasible alternative for larger-size particles) will be preceded by evaluations of their validity, and fine-tuning, if needed. The evaluations will be made against the results of select accurate all-electron computations.

Gradient-based techniques applied to a sufficiently large number of initial guess configurations will be used to find stationary structures of the particles. The procedure will involve no symmetry constraints, i.e., it will be applied to all the degrees of freedom. Normal mode analysis will be performed to filter out those stationary structures that represent saddles (transition state configurations), rather than minima (globally or locally stable equilibrium structures), of the corresponding potential energy surfaces. These studies will be carried out for those metal (e.g., silver, gold, etc.) particles, which will be the subject of the electrodynamics studies described in Sect. III.A. Their central role will be to obtain the different, possibly competing, structural forms of the clusters and their electronic characteristics. The latter will include the binding energies and the one-electron energy spectra, as well as the response functions such as polarizabilty and dielectric characteristics (see below). An important aspect of the studies will be to establish the correlation between the structural and electronic characteristics as a function of the particle material(s) and size. In addition to the bare metal particles the computations will also include particles coated by judiciously chosen ligands (cf. the discussion in Sect. A.1).

The size-dependence will be an omnipresent theme. We intend to cover a relatively broad range (from a few, or few tens of, atoms to a few hundreds of atoms), which will include the regime where the properties change with the size nonmonotonically and where the particles exhibit truly unique and often unexpected features. It is these novel features that hold the promise of revolutionizing many technologies, including the ones that relate to photonic and electronic transport. Our goal is a comprehensive understanding of the interdependence of the structural, electronic, and optical properties. For example, as has been mentioned in Sect. II, atomic clusters of metallic elements acquire metallic characteristics as they grow in size. This transition to metallicity is a consequence of the size-driven changes in electronic structure, which are coupled with and depend on, as well as influence, the structural changes. An intriguing and important for applications question, which we intend to address is: what is the relationship, if any, between the size-induced transition to metallicity and the optical (response) characteristics of nanosized metal particles?

The role of high-level, accurate theoretical/computational studies in answering the above-mentioned issues is central. At present, some of these can be addressed and answered only through theoretical/computational means. An example is the structures of metal particles in the small and intermediate size regime and their effect(s) on the electronic and optical properties. The reason for this is that experimental determination of and discrimination between the structures in this size regime is a problem yet to be solved. The DFT

computations involved in these studies, especially for particles with a few hundreds of atoms, are very demanding. Optimizations of the codes and use of parallel processing will be imperative (See Sec. III.B).

Development of accurate semiempirical many-bod potentials. Even with optimizations and use of parallel computers the types of DFT studies described above cannot be extended to metal nanoparticles with thousands and more atoms. This is true at present and will remain true for an observable future. An alternative is to use semiempirical many-body potentials that accurately describe the interatomic interactions in the particles of interest. In the hierarchy of the theoretical/computational tools these potentials fulfill an important role. Although they contain no explicit information on the electronic and optical properties, except that the total electronic energy is part of the configurational energy represented by them, they allow for very efficient exploration of the structural and dynamical (thermal) properties of systems with tens and hundreds of thousands of atoms. In the context of the present work we will use these potentials for two principal goals. The first is to obtain the structural forms of large metal nanoparticles both in the gas phase and deposited on substrates; in the latter case the interactions with the atoms of the substrate will explicitly be included. The second goal is to explore the thermal properties of these particles, on the one hand, and the mechanism of their assembly into different nanoarchitectures, on the other (see below).

The accuracy of the results obtained using these potentials depends on their quality. Therefore construction of more accurate parameterized many-body potentials is a task of first rate importance. We will address this task by examining both the choice of the functional form(s) and performing a more adequate optimization of the adjustable parameters. This will be done for all the metals of interest. A good starting guess for the functional form is the so-called Gupta-type potential [60, 106], which is based on the second moment approximation to the tight-binding model. The optimization of the parameters will be performed using our minimal maximum error fitting procedure [60]. The set of fitting properties will include data that represent bulk features, properties of the diatomic molecule, and of different-size clusters of the metal. Both measured and computed quantities, including those obtained in DFT computations described above, will be used in the fitting set.

Studies of thermal stability and nanoarchitecture assembly. An important practical consideration regarding any nanodevice is its thermal stability (energy dissipation into heat eitherin photonic or electronic transport is unavoidable even at the nanoscale). We will address this issue using dynamical (MD) and statistical (MC) analyses. Whereas DFT-computed energies and forces can be used for this in the case of small systems, the bulk of the studies will employ the fitted semiempirical potentials discussed above. We have extensive expertise and experience in studies of thermal properties of finite systems, in general, and metal clusters, in particular [40, 41, 46-51, 58, 59]. We will use these to characterize the different stages in the heat-induced structural changes (including the melting transition) both in different metal clusters/nanoparticles and the nanoarchitectures assembled from them.

The assembly into nanoarchitectures will be studied dynamically (MD). We will explore both the atom-based and the cluster-based routes. In the first, we will simulate metal atom deposition on substrates of interest, diffusion of the atoms and their eventual aggregation into nanoparticles and nanoarchitectures. The size, shape, and architecture of the resulting aggregates will be studied as a function of the material(s) of the substrate and the “topography” of its surface (e.g., lithographically engineered grooves and holes, steps, kinks, defects, etc.) In the second, clusters/nanoparticles of a given composition and size(s) will be used as the primary building blocks. Experimental evidence suggests that both the composition and the size

of these building blocks have a major effect on the outcome of the nanoassembly [107, 108]. For example, as characterized by their geometric dimensionality, they may have usual integer-valued dimensions or be fractal objects (e.g., of dendritic form). Our central goal is to understand how characteristics such as the strength of the interaction between the metal atoms, or particles, vs that between atoms/particles and the substrate and the steric effect(s) due to the particle size define and affect the mechanisms of nanoassembly. This understanding will allow us to suggest ways for a controlled assembly of nanostructures with tailored characteristics. The potential use of these systems as chemical or biological sensors, and other possible nanophotonics aspects, will be investigated with the methods of Sec. III.A.1.

Optical response of metal clusters and nanoparticles. For macroscopic materials, the response to electromagnetic oscillations is described via the frequency-dependent dielectric function, which relates the average electric field inside the material to the external driving field. The internal field combines the external field and contributions due to the polarization of the atoms in the sample. The averaging is done over an atomically large (i.e. nanoscale), but macroscopically very small region of the material. In nanoscale systems, the macroscopic concept of the dielectric constant loses its meaning and the dynamic polarizability $\alpha(\omega)$ becomes the key quantity of interest. The focus of this portion of the project will be on using state-of-the-art electronic structure techniques to study the dielectric response of metal nanoparticles, and how this response varies with characteristics such as particle shape and size. The information on the dielectric response will serve as an essential input for some of the calculations modeling the propagation of electromagnetic waves in nanoscale systems as described in Sec. III.A.1 above.

The electronic structure work will be based on DFT methods. The overall approach will be to use DFT calculations to directly and systematically model the response of small atomic clusters ($n \leq 100$), and, based on those results, to develop reliable empirical models for treating the dielectric response of larger particles extending well into the nanoscale. The DFT calculations can be broken into two categories, static and dynamic, corresponding to the static and frequency-dependent response of the system, respectively. We have extensive experience with both types of calculations [67,68,75,77,78,80,81] and are well-positioned to undertake the work proposed here.

The methodology for computing the static polarizability of a cluster is well-established. The expansion of the DFT cluster total energy as a function of an applied external electric field, **F,** reads:

$$E(\mathbf{F}) = E(0) - \mu\cdot\mathbf{F} - (1/2)\,\mathbf{F}\cdot\alpha\cdot\mathbf{F} + \ldots$$

where μ is the cluster electric dipole moment and α is the electric polarizability tensor**.** These latter quantities can thus be defined in terms of derivatives of the cluster total energy with respect to the external field:

$$\mu_i = -\partial E/\partial F_i|_{\mathbf{F}=0} \quad ,$$

$$\alpha_{ij} = -\partial^2 E/\partial F_i \partial F_j|_{\mathbf{F}=0} = \partial\mu_i/\partial F_j\,.$$

A spatially uniform external electric field **F** adds a term $V_{ext} = -\mathbf{F}\cdot\mathbf{r}$ to the effective potential seen by the electrons in the Kohn-Sham (KS) equations:

$$(-\nabla^2/2 + V_{Ion} + V_{Coul} + V_{xc} + V_{ext})\,\phi_i = \varepsilon_i\phi_I\,.$$

Including the external field in a finite cluster calculation is straightforward, and has been fully implemented in our DFT codes [68,75]. After solving the above equation self-consistently, the orbitals are used to construct the total energy, E[**F**], and the cluster dipole moment, μ[**F**], as functions of the external field. Derivatives with respect to the external field can be computed by finite differences, using the results of independent self-consistent calculations using different values of the field. Field strength differences of 0.005 a.u. yield reliable results for the polarizability [68,75]. One objective will be to compute the average polarizability per atom, α, systematically for metal particles over a range of cluster sizes and shapes, and to correlate α to these latter. We found systematic changes in α as a function of the shape of Si clusters. Prolate structures turned out to be more polarizable than more spherical compact structures, a result attributed to a large number of relatively weaker bonds in the prolate clusters [68].

The Clausius-Mossotti equation relates the macroscopic dielectric constant of a solid to the average atomic polarizability:

$$\alpha = [3/4\pi]\ ((\varepsilon-1)/(\varepsilon+2))v_{at},$$

where ε is the static dielectric constant and v_{at} is the atomic volume in the solid. We can use this equation to compare the response of the nanoparticles to that of corresponding bulk solids. In the case of Si clusters, for example, the clusters are found to be more polarizable than the bulk, and approaches the bulk limit from above with increasing cluster size [67,75].

Computing as a derivative of μ also allows us to determine the polarizability as a function of the position within the cluster. To determine the polarizability of the surface layer of atoms, for example, one integrates the charge only over the volume corresponding to the outer layer to get the dipole associated with that layer. The surface polarizability is then found from the change in the surface dipole with the external field.

We will extend our polarizability calculations to the time dependent regime, using time-dependent density functional theory (TDDFT) methods [109]. The static DFT is intrinsically a ground state theory, hence does not work well for excited state properties (poor excitation energies, band gap problem in semiconductors are just a few relevant examples). Over the last decade, TDDFT, on the other hand, has proven to be a computationally quite efficient and accurate method for investigating excited state properties in confined systems such as clusters. In calculating the frequency-dependent polarizability $\alpha(\omega)$, one cannot make use of the total energy expansion above, as this relationship exists only for $\omega = 0$. Instead, the time-dependent external field has to be explicitly included into the formalism, and this can be achieved using TDDFT. We have extensive experience with the implementation of this formalism, having applied it to the calculation of excitation energies, dynamic polarizabilities $\alpha(\omega)$, photoabsorption cross sections ( ) of atoms, molecules, clusters, and nanocrystals up to a few hundred atoms [77,78,80,81].

In TDDFT, one solves the time-dependent version of the KS equation to examine the effect of an external time-periodic perturbation $E(t)=E_0e^{i\omega t}$. This can be done in either real time by integrating the KS equations at discrete time steps [100, 111] or in frequency space. For the calculations proposed here, we will use TDDFT in the frequency domain within the adiabatic local density approximation (TDLDA). We will also investigate the effect of asymptotically correcting the exchange-

correlation kernels.

The full TDLDA formalism can be found in the literature [109] and in our earlier studies [77,78,80,81]. In TDLDA, the system response to an external time-dependent perturbation is described by a coupling matrix K, which is constructed from the ground-state Kohn-Sham wavefunctions and Hartree, exchange-correlation potentials. This coupling matrix can then be used in the construction of a new matrix Ω, whose eigenvalues give the the square of collective excitation energies Ω_I, while the eigenvectors are related to the oscillator strengths f_I for the particular excitation energy. When the exact TDLDA matrix Ω, which includes all collective excitations, is used to calculate the excitation energies, the agreement between the theoretical and experimental results improves significantly compared to the single particle excitation energies obtained from static DFT calculations.

Once the collective excitation energies and oscillator strengths for these transitions are calculated, the dynamical polarizability $\alpha(\omega)$ is obtained through $\alpha(\omega)=\Sigma\, f_I /(\Omega_I^2 - \omega^2)$, where the sum is over all collective excitations. The dynamical polarizability calculated in this fashion for $\omega=0$ should agree with the static polarizability calculated using the finite-field method explained above. This has indeed been shown to be the case for a variety of small clusters in our previous work [77,78,80,81]. The oscillator strengths f_I and the collective excitation energies, such as the plasmon peaks in metallic clusters, can be used to calculate the total photoabsorption cross section $\sigma(\omega)$, which is related to the imaginary part of $\alpha(\omega)$. In our previous work, the calculated cross sections for various semiconductor and metallic clusters have yielded very good agreement with experimental results, especially when the TDLDA calculations were compared with excitation energies calculated from static DFT calculations, as mentioned above.

The incorrect (exponential) asymptotic behavior of the LDA exchange-correlation potential (in contrast to the exact 1/r behavior) may cause inaccuracies in the calculated response functions. Therefore, we will test our LDA-based results on the dynamical polarizability against those obtained with asymptotically correct functionals [112-114].

Another focus point will be the calculation of the microscopic dielectric response function $\varepsilon(\mathbf{r}_1,\mathbf{r}_2,\omega)$. Recently, we developed an efficient real-space approach for accurate calculation (and storage) of the wavevector-dependent, yet static, dielectric matrix $\varepsilon(\mathbf{r}_1,\mathbf{r}_2)$ and its inverse $\varepsilon^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ suitable for large confined systems [83]. The method relies on the separability of the dielectric matrix in $\mathbf{r}_1$ and $\mathbf{r}_2$, by expressing it as a sum of the identity matrix plus an outer product of two low-rank matrices. This approach has allowed for the first time efficient calculations of *ab initio* dielectric matrices with dimensions as large as 270,000 and for quantum dots as large as $Si_{35}H_{36}$. Based on these first principles calculations, we constructed spatially dependent model dielectric function $\varepsilon_M(r)$, which resulted in quite accurate exciton Coulomb energies for the screened electron-hole interaction. The extension of this method to the frequency-dependent case is quite straightforward, and we intend to implement it for metallic clusters within the framework of this proposal. This will allow us to investigate both the spatial and the temporal response of the systems in a computationally efficient way. Accurate model dielectric functions based on these ab initio calculations will be developed. Based on the collaborative and interdisciplinary nature of the work proposed here, we intend to investigate dynamical polarizabilities and absorption spectra of Ag_n and Au_n clusters with n up to about 150. These results will allow us to extrapolate to particles whose size extends into the range of tens of nanometers.

So far we have focused mostly on relatively simple metal nanoparticle systems. Regarding more complex, hybrid systems, we propose to incorporate the non-local linear responses into electrodynamics of semiconductor QD/metal nanoparticle complexes and clusters of densely packed metal particles. The necessity of such incorporation is dictated by the fact that the relevant distances for QDs (their radius and distance from the metal surface) are $a \approx 1$ nm. This distance is comparable to the Debye (or, Thomas-Fermi) screening radius at the surfaces of metal nanoparticles and is much smaller than the electron mean free path in metals. This indicates that the interaction of QDs with metal nanoparticles may be essentially non-local. For nanoclusters of closely spaced nanospheres at distances between the surfaces of nanospheres $a \approx 1$ nm, the non-locality will also be important for the same reasons as for QDs. Additionally, very high number of spherical harmonics will be needed, estimated as R/a , where R is the nanosphere radius. Our approach will be to employ the quasiclassical Thomas-Fermi approximation, or a quantum mechanical Local Density Approximation (LDA) to describe the electron density in a nanoparticle. The linear response to the excitation field on the nanoscale will be determined on this basis from the well-tested Random Phase Approximation (RPA). Note that a similar program has been so far implemented only with respect to thin metal nano-shells [115]. The resulting susceptibilities will be averaged over an intermediate scale and input into the macroscopic electrodynamics programs. One of the important problems that has not yet been earlier considered is the effect of the close proximity to a metal nanoparticle on electronic and optical properties of QDs. We anticipate that the metal nanoparticle will significantly increase both the dipole strength of the QD transition (due to enhanced local fields – so called nanoantenna effect) and the rate of relaxation. Due to small distances ($a \approx 1$ nm) involved, these effects cannot be reliable treated on the basis of the macroscopic dielectric response. Instead, the above-outlined microscopic method will be employed. This part of research is of particular relevance to the physics of electronic and photonic devices based on QDs and metal components such as QD lasers and spasers, QD computation and memory chips, etc.

B. Applied Mathematics and Software Development

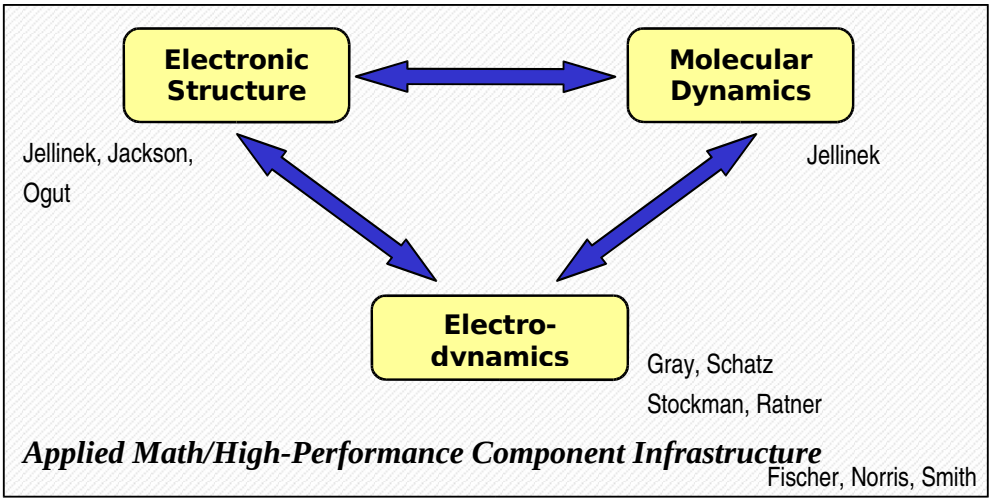

Figure 3. Schematic diagram of NSTOP.

Sections III.A.1 and III.A.2 discussed many explicit theoretical modeling approaches, that involve applied mathematics problems for which the MCS co-PIs will be involved. However we hope to use the experience and the codes that result to construct a general suite of nanophotonics codes, NSTOP. NSTOP will contain many different software components associated with different modeling scales for nanophotonics. As sketched in Fig. 3, NSTOP will contain electronic structure codes to provide basic electronic and material information, molecular dynamics codes to carry out simulations of the assembly of various nanoarchitectures and electrodynamics codes to carry out modeling of how light interacts with given nanoarchitectures. The double arrows in the figure indicate there can be "communication" between the three broad areas above, i.e. a calculation at one level might suggest new calculations at a different level. Of course there can also be more active forms of communication, e.g. and MD calculation progressing by repeatedly interacting with the electronic structure level.

Since nanophotonics simulation is still a relatively new area, it is not yet clear exactly which models and algorithms will be most efficacious. Thus, extensibility is a paramount aspect of the software design of NSTOP codes. We will use existing numerical packages, such as PETSc and Chombo, in our implementation in order to achieve robustness and high performance. We will also develop new numerical

methods specifically targeting the needs of nanophotonics applications. Furthermore, to enable interoperability and code reuse, we plan to implement NSTOP codes as components.

The MCS group has extensive experience in developing general-purpose code that can be adapted easily for specific problems. We will leverage this experience by using PETSc (Portable, Extensible Toolkit for Scientific Computation) for providing numerical solutions and parallelization of many of our scientific codes. (See http://www.mcs.anl.gov/petsc/petsc-2/publications.) PETSc has already been used successfully for the FDTD codes in two dimensions. PETSc's parallel linear solvers will also be used in the DDA, T-matrix, and Green's function methods, which require the solution of very large linear systems. For example, for DDA calculations, converged results of metallic structures can be obtained if the element size is roughly 2 nm in each dimension. An object with 200 nm dimensions in each direction requires 10^6 elements, which is not solvable with the current implementation (Gaussian elimination or complex conjugate gradient methods). To accommodate large problem sizes and better scalability, we will employ the PETSc suite of Krylov subspace methods, a set of well-tested general-purpose parallel solvers that have been used in dozens of application areas on problems with up to 32 million degrees of freedom.

Even at the classical, continuum level of description, the electromagnetic fields consistent with metal nanoparticles interacting with optical wavelengths are very challenging to model accurately owing to a variety of length scales being operative. The overall system size must be on the order of several wavelengths of the applied light, e.g. for 500 nm wavelength light, length scales of, say, 2000 nm, should be considered. However, the metal nanoparticles are typically of dimensions on the order of 20-50 nm and, furthermore, the fields undergo extremely abrupt changes and achieve remarkably high magnitudes over a tiny region on the order of 1 nm in the vicinity of the surfaces of the particles. We now outline pseudospectral and meshing approaches that we believe will make an impact on the efficiencies and capabilities of several of our electrodynamics components in NSTOP. Actually, the electronic structure methods discussed in III.A.2, being based on real space density functional theory, should also benefit from these considerations.

A central component of our numerical electrodynamics modeling will be the use multidomain spectral methods, which are capable of treating complex domains, variable coefficients, and a variety of boundary conditions, all with a maximum of efficiency. Traditional second-order FDTD approaches, for example, require a spatial resolution of roughly 20 points per wavelength in each direction, while classical Fourier pseudospectral approaches require only 2 points per wavelength. Multidomain spectral methods based on Legendre or Chebyshev polynomials offer significant flexibility over Fourier or high-order finite difference methods and require roughly points per wavelength - a small fraction away from the optimal (2) dictated by the Nyquist criterion. Moreover, the accuracy of the transmission for the resolved waves converges exponentially fast with increasing polynomial order, N. Spectral methods thus offer the accuracy required for long time integrations, or equivalently, propagation of short waves over long distances. In this context, we will investigate the use of high-order Whitney forms [116], which preserve symmetries intrinsic to Maxwell's equations. We will develop codes that make the preservation of these symmetries as a run-time option, so that users may test the accuracy/efficiency trade-offs of these approaches on a case-by-case basis. These codes will be compatible with the Terascale Simulation Tools and Technology (TSTT) interface, which will allow them to be interoperable with several existing mesh packages. Multidomain spectral methods have been used in electromagnetics computations by the group at Brown [117,118] and Paris VI [119] The MCS group has significant experience in the development of multidomain spectral methods [86-88] and in terascale applications of these methods on thousands of

processors [89].

To accommodate the large number of degrees of freedom characterizing 3D FDTD codes, we will use the adaptive mesh refinement package Chombo whose development is supported by the SciDAC Applied Partial Differential Equations Center (APDEC). Chombo provides a distributed infrastructure for implementing finite difference methods for the solution of partial differential equations on block-structured adaptively refined rectangular grids. Both elliptic and time-dependent models are included. There is also support for multigrid where appropriate. Chombo is ideally suited for resolving the multiple-length scales very near the nano-particals and will allow computations with well over 10 million degrees of freedom. Furthermore, Chombo's design is uniquely flexible and accessible, and thus well suited for use in NSTOP codes. Depending on need, we may experiment with using implicit methods for the Maxwell's equations using PETSc in concert with Chombo, but likely explicit methods will suffice. (See http://www.seesar.lbl.gov/ANAG/chombo/.)

In addition to leveraging existing numerical packages, we will organize NSTOP into a suite of components compliant with the Common Component Architecture (CCA) definition and using the infrastructure developed as part of the SciDAC Center for Component Technology for Terascale Simulation Software (CCTTSS). (See http://www.cca-forum.org.) We will rely on the experience of MCS co-PIs who have been actively involved in the development of numerical components and component infrastructure. Public interfaces for NSTOP components will be defined using the Scientific Interface Definition Language (SIDL). (See http://www.llnl.gov/CASC/components.) SIDL allows different subsets of the software to be written in any one of a set of supported languages, including C++, Fortran 90, Python, Matlab, and Mathematica, and used seamlessly from another language. We note that our co-PI Smith is leading the effort in adding SIDL interfaces to PETSc (and thus multilingual support) and will bring this expertise to the NSTOP development effort. MCS co-PIs will coordinate the effort in defining the hierarchy of interfaces governing the interactions among NSTOP components. Defining SIDL interfaces and implementing NSTOP codes as CCA components will enable the "plug-and-play" assembly of applications out of components providing model descriptions, numerical solvers, mesh management, visualization, etc. We will also analyze and fine-tune the performance of NSTOP components whenever appropriate, using tools such as those developed in the SciDAC Performance Evaluation Research Center (http://perc.nersc.gov/). Finally, the NSTOP suite of components and applications will be made available to researchers in nanophotonics via an on-line repository.

C. Summary and Anticipated Major Research Progress

The self-assembled team of PIs has broad expertise in all the required scientific and computational issues that must be addressed over the years if the proposed program is to be successful, i.e., have a large impact on the nanoscience and computational science communities. It consists of National Laboratory scientists (Gray, Jellinek), and applied mathematicians and computer scientists (Smith, Fischer, Norris), teamed up teamed up with academic experts (Schatz, Ratner, Stockman, Jackson, Ogut).

We have proposed a variety of scientific studies, ranging from electronic structure level calculations to continuum level electrodynamics simulations. A variety of systems will also be studied, ranging from small metal nanoclusters up to metal nanoparticles with spatial dimensions of 50 nm, as well as more sophisticated hybrid systems involving also, e.g., quantum dots and molecular wires. We have also

proposed a challenging software/applied mathematics program that will lead to NSTOP, a comprehensive suite of state-of-the-art simulations tools for general use within the nanophotonics and general nanoscience communities. The scientific and applied mathematics/computer science issues are of course intimately entwined, particularly for the largest simulations we propose to do which will require incorporation and development of the best numerical methods and high performance computing issues.

Aspects of the project will obviously evolve over the course of its existence, particularly since the area is young and effervescent, with new experimental and theoretical results being published at a breath-taking pace. The anticipated major research progress we now outline is thus forward-looking, based on our current understanding of the science and computational issues.

Initial Phase (Years 1 - 2):

- Develop parallel, scalable versions of all the key codes in this proposal: electrodynamics codes based on FDTD, DDA, T-matrix, or Green's Function, electronic structure codes based on DFT, and dynamics and assembly codes based on MD. Key to this parallelization will be PETSc parallel solvers, including specialized solvers within the PETSc framework.

- Develop advanced numerical methods, within the context of scalable parallelization, on a code by code basis. Adaptive mesh refinements via Chombo or other methods will be applied to mesh based codes (e.g. FDTD or DFT). Multidomain pseudospectral techniques will be investigated for several of the electrodynamics codes (e.g. FDTD or T-matrix). Novel iterative eigensolvers or linear solvers will be examined for several codes (e.g., Green's Function or DFT).

- DDA simulations that include semiconductor features (e.g., dipole-emitters in the presence of polarizable elements).

- Nonlocal dielectric response of QDs interacting with metal nanoparticles will be deduced with DFT methods.

- Develop a fundamental theory and computational method for the interaction of SP excitations with molecular wires (mixed quantum/electrodynamics simulations via Landauer theory coupled with applied fields).

- DFT studies of structural, electronic and optical response properties of bare and ligand-coated metal clusters/nanoparticles over the size range covering tens to hundreds of atoms.

- Work on the construction of more accurate semiempirical many-body potentials for metallic systems and use of these in large-scale MD studies of structural and thermal properties of nanoparticles over a broad size range (thousands - tens of thousands of atoms).

- SIDL interface definition for NSTOP codes; preliminary CCA-compliant implementations of several of the dynamics and electronic structure codes.

Final Phase (Years 3-5):

- Develop a robust, scalable, extensible, and portable NSTOP suite of codes. Incorporating SIDL interfaces and provided as CCA components, NSTOP will go on line via ANL websites component by component to allow testing and input from the nanophotonics community. It is the intention of this proposal that NSTOP will become a software basis for the growing nanophotonics simulation community.

- Test and verify the usefulness and efficiency of NSTOP by performing a series of challenging and diverse set of studies that will include:

  Our first "cradle to grave" study of a small Ag metal nanoparticle, uniting contributions from all PIs: Electronic structure and MD studies to learn optical and structural features, and a detailed examination of spectral (e.g., absorption) and other properties using our FDTD and various frequency-domain electrodynamics programs.

  Realistic modeling of AFM tip/metal nanoparticle/surface interactions via FDTD and other techniques.

  Large-scale simulations and analysis of the mechanisms that drive atom-based and cluster-based assembly of metallic nanoarchitectures that display important photonic properties.

  Realistic 3D simulations of nanoparticle metal arrays interacting with quantum dots and/or molecular wires.

  Electrodynamics simulations of spherical particles and arrays of truncated tetrahedrons of relevence to nanosphere lithography.

- Perform large-scale simulations and develop and understanding of the mechanisms that drive atom-based and cluster-based assembly of metallic nanoarchitectures and their photonic properties.

- Add realistic models of quantum dots into the FDTD code, GF code and other simulations codes; initiate simulations.

- Simulations codes capable of modeling of light propagation through metal nanoparticles and molecular wire junctions will have been developed and tested.

An important component of all the activities within this proposal will be the training of young scientists at the post-doctoral level and training and education of students at the graduate level as specified in the budget pages.

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BUDGET AND BUDGET EXPLANATION

OTHER SUPPORT OF INVESTIGATORS

BIOGRAPHICAL SKETCHES

DESCRIPTION OF FACILITIES AND RESOURCES

The PIs either own or have access to the considerable computational resources needed for this work. These include a 50-processor Pentium III Linux cluster (Gray), a 128-processor Pentium IV Linux cluster (Jellinek), as well as access to the JAZZ 350 processor Linux cluster of MCS, and the high performance computing facilities at NERSC.

1. Group Computer Facilities:

Each of the principal investigators has a variety of group computer facilities available to them ranging from workstations to modestly large Linux clusters of 50 (Gray) and 128 (Jellinek) nodes. To facilitate the work of this proposal, accounts will be set up on a variety of machines at multiple institutions to allow each investigator broad access to a variety of group-scale computers.

2. Laboratory Scale Computer Facilities

Argonne National Laboratory operates a Laboratory Computing Resource Center (LCRC) that currently supports one terascale linux cluster called Jazz. Jazz has 350 nodes, each with a 2.4 Ghz Pentium Xeon CPU. Half the nodes have 2 GB of RAM and half have 1 GB of RAM. Myrinet 2000 provides the network. The disk systems holds 20 TD of data. Jazz is accessible to ANL staff and their collaborators with resource allocations provided by review of written request. The LCRC will be the major computer component of the Argonne Center for Nanoscale Materials, one of five Nanoscience Research Centers sponsored by DOE. At the highest laboratory level, there is a commitment to use the LCRC to facilitate nanoscience simulations. During the lifetime of this proposal, the LCRC will grow beyond the current Jazz machine and one of the drivers of that growth will be nanoscience simulations as exemplified in this proposal.

3. National Computer Facilites

The National Energy Research Supercomputer Center (NERSC) maintains a truely massive parallel computer facility. At present, the main machine called Seaborg is a 6,656 processor IBM RS/6000 SP with 416 16-CPU POWER3+ SMP nodes. It has 7.8 TB of aggregate memory and 44 TB of disk storage. Seaborg is the largest computer in the United States for unclassified research. The ANL investigators have accounts on Seaborg and other NERSC computer facilities. If this proposal were funded , the largest computations would be performed here.