Modeling nanomaterial physical properties: theory and simulation

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\section*{ABSTRACT}
A brief theory and simulation overview for the purpose of design is presented with examples applies to modeling the physical properties, behavior, and phenomena of nanomaterial. This review paper constructs perspectives that consider coupling traditional domains of simulation by novel pathways to produce accurate representations of nanomaterial properties, behavior and phenomena. It is all about size scaling and how different approaches are able to simulate, integrate or simply pass the baton to the next level of complexity. In macroscopic world, the atomic or molecular information alone may not be directly useful. Nor is the bulk information useful in the microscopic world without intimate knowledge of molecular makeup. Therefore, when designing Nanomaterials, knowledge of properties spanning the complete range of size is the prerequisite of a recommended self-consistent approach. In fact, regarding applications in both industry and academia, the simulation first approach often can lead to great savings in time. This review paper focuses mostly on optical and electronic properties but a section is added that provides a segue into mechanical properties for future consideration.

\section*{Introduction}
Material simulation methodologies have become powerful tools for scientists and engineers especially now with the advent of faster computing capability and sophisticated computer programs. The complete spectrum of size dependent properties and behaviors can be modeled with great confidence. Ideally, and theoretically, modeling everything from first principles would be a boon to the material simulation community, however, due to limited computing capability, this approach is still off into the future. Nonetheless, several bold computational and numerical (and hybrid) methods, originating from dramatically differing
perspectives based on bold assumptions, have been developed to circumvent the aforementioned limitations.

Significant progress has been made over the past decade in coupling classical Maxwell’s equations to other established simulation approaches, especially in the area of predicting nanoscale plasmonic and optical properties [1]. Maxwell-Schrödinger equation hybrid systems have been created and solved by a unified Hamiltonian approach capable of simulating classical electromagnetic fields and particles [2]. Authors of this paper proposed a coupled method based on a unified Hamiltonian of electromagnetic and quantum mechanics. The numerical methods of modified Finite Difference Time Domain (FDTD) was then applied to overcome discrepancies between wavelength dependent electromagnetic properties and those of electron waves [2]. The result yields a useful hybrid method with coupled classical electromagnetic, quantum mechanics and numerical methods. This method was then used to simulation nanomaterials and nanodevices, including those based on quantum mechanics. In particular, the coupling of finite element methods (FEM) with classical Maxwell’s equations based methods leads to the direct computation of Maxwell equation, which has made a headway into modeling nanomaterials [3]. Recent developments in nanoscience and nanotechnology, among other fields, ‘have made it possible to conceive materials and structures with atomic level controllability and with unprecedented properties…. These developments have opened doors to shape and sculpt light at the nano-, micro and mesoscales in a desired fashion’ [4]. A new numerical method, ‘Extended’ Finite-Difference Time-Domain (EFDTD) method, has been developed to analyze nanoscale systems [5]. EFDTD is used to solve Maxwell’s equations in combination with Schrödinger’s equation to evaluate quantum effects such as those encountered in electron tunneling through potential barriers. For future nanoscale circuit design and analysis, an important role would be played by such approaches that can consider all physical interactions to compute and model [5].

There are a wide variety of programs at hand for the researchers and engineers, both commercially available and via open source. These include cross-platform finite element programs for multi-physics simulation that are capable of solving for coupled phenomena. For example, fluid dynamics coupled with heat transfer. Current molecular domain simulations are capable of linking material atomic and molecular structure with their microscopic properties and behavior. Varied simulation approaches based on fundamentally different premises can effectively work together to model material behavior, especially in the case of nanomaterials. For example, classical electromagnetic (EM) and thermodynamic theories can provide inputs for methods that have completely divergent and unrelated theoretical roots; for example, inputs into numerical convergent methods. Quantum physics based methods such as density functional theory (DFT) are capable of providing such fundamental data into classical EM equations. Here we show examples of such coupled and/or convergent efforts in the simulation of optical properties and of plasmonic systems. Simulations of mechanical systems, which is deeply rooted in finite element methods, are provided at the conclusion of the paper.

**Size domains**

Classical approaches of course are still valid as stand-alone methods that can adequately predict nanomaterial properties, optical properties in particular. We consider three
conventional and conveniently defined size domains. Macroscopic material properties can be described by either classical geometric optics or electromagnetic wave theory without input of atomic or molecular information or consideration of localized material interactions with photons and electrons \([6]\). We and many others have shown that classical electromagnetic approaches can be very useful in predicting nanoscale material optical properties through the lens of macroscopic observables – i.e. as in the case of composite materials \([7,8]\). Effective medium theories and scattering matrix approximations, applied without further input into finite element systems, have proven to be of great value in predicting optical properties of composite materials and periodic arrays, photonic structures, respectively \([6]\). Therefore, to a point defined by macroscopic size limits, classical representations are completely valid and useful.

Regarding the microscopic perspective, atomistic-molecular approaches are traditionally represented by \textit{ab initio}, molecular dynamic, density functional theory (DFT), Monte Carlo and tight-binding combinations among each other – essentially modeling physical properties from the bottom up. In principle, information based within quantum mechanics contains all relevant information about any material system. However, the exact analytical solution to the Schrödinger’s equation are almost impossible for any \(N\)-body system and we have to invoke approximations to help us along. DFT in particular offers such an approach to solving Schrödinger’s equation for multiple-particle systems by providing an approximate method that correlates motions of electrons. The non-relativistic time-independent Schrödinger equation is given as,

\[\hat{H}\psi = E\psi,\]

where \(\hat{H}\) is the Hamiltonian or total energy operator, \(\psi\) is the wavefunction describing the system and \(E\) is the energy. DFT reformulates the Schrödinger equation into the Kohn-Sham equations:

\[\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(r)\right)\phi_i(r) = \epsilon_i\phi_i(r),\]

where \(\{\phi_i(r)\}\) is a set of single particle orbitals representing fictitious non-interacting electrons. The ground state electron density calculated from the orbitals \(\rho(r) = \sum_i |\phi_i(r)|^2\) is a central quantity in DFT. It uniquely determines the Hamiltonian operator from which all the properties of the system’s ground state can be deduced. The Kohn-Sham effective potential is given by:

\[V_{\text{eff}}(r) = V_{\text{Ne}} + \frac{\delta J[\rho(r)]}{\delta \rho} + \frac{\delta E_{\text{XC}}[\rho(r)]}{\delta \rho}\]

In this formulation the total energy can be written as:

\[E[\rho(r)] = V_{\text{Ne}}[\rho(r)] + T_S[\rho(r)] + J[\rho(r)] + E_{\text{XC}}[\rho(r)],\]

where \(V_{\text{Ne}}[\rho(r)]\) is a functional representing the nuclear-electron attraction potential energy, \(T_S[\rho(r)]\) is the exact kinetic energy of the non-interacting fictitious reference system with the same density as the real interacting one. \(J[\rho(r)]\) represents the classical
contribution to the electron-electron interaction. And $E_{XC}[\rho(r)]$ is the correlation-exchange energy. The Kohn-Sham equations are exact, however, DFT is necessarily made approximate by the fact that the explicit and exact form of the exchange correlation functional is not known. However, accurate approximations for $E_{XC}$ are possible and eventually yield correct quantitative results.

From such DFT approximations, structural and electromagnetic characteristics of materials can be investigated. As such, DFT has become one of the most popular and resourceful methods in condensed matter and computational physics. In fact, DFT has successfully provided quantum modeling of optical properties of nanomaterials as well as structural information relating to phase diagrams [9]. However, DFT is still complicated and therefore the FEM is introduced to simplify the simulation. FEM and facilitative adapted versions are now used solve Kohn-Sham equations of DFT to provide realistic three-dimensional representations [9].

Lastly, at the mesoscopic domain within which nanomaterials reside, applies electromagnetic tools that are superimposed upon some preconceived nanoscale scaffolding [10]. Particles ranging in size from 1 to 100 nm are considered to be nanoparticles. Nanomaterials have a countable number of atoms and are Par Excellence substrates for current $N$-body problem solving programs. They also are well-suited to occupy the position of the fictitious mesoscopic bipolar cavity envisioned by early electromagnetic theoreticians to justify linking Maxwell’s equations to the macroscopic world. As stated earlier, atomistic-molecular parameters are not always considered in simulations. Input of bulk material derived optical constants are routinely input into classical (and FEM) programs from which nanomaterial properties are predicted. However, for decades, combined methods utilizing molecular dynamic simulations and the finite element method have begun to provide simultaneous resolutions at the atomistic-molecular and continuum field scales [11]. Furthermore, finite element methods have been applied to the atomic scale via ‘multiscale simulations’ in the development of nanotechnology by providing seamless and facilitated computation [12].

Finite element numerical methods, assuming importance in the early seventies, were derived mainly to solve macroscopic engineering problems [13]. However, today, finite elements can be applied even down to the molecular scale. Natural phenomena show multiscale character in space and time. ‘Continuum-on-atomistic’ multiscale coupling methods have achieved great popularity today [14]. Actually, when considering electromagnetic input parameters, finite element methods are able now to stand alone when describing optical properties of nanoscale structures [15].

**Optical properties of nanomaterials by classical EM and FEM**

**Classical treatments**

Efforts have been made since Maxwell’s equations were established to explain electromagnetic theory from the atomic level – i.e. to link the microscopic with the macroscopic. However, at the microscopic level, molecular dipole fields are discrete (not smooth) and variant over molecular dimensions and timescales – not exactly suitable for treatment by classical electromagnetic theory. Therefore, the fictitious mesoscopic cavity was invented to average molecular microscopic fields over larger size scales and
lengthier timescales – albeit with dimensions significantly less than of a macroscopic material [6]. Resultantly, the constitutive material equations are required to link Maxwell’s equations to the macroscopic world via the relative dielectric function $\varepsilon_r$. Following O-F. Mossotti’s view of dielectric behavior, Maxwell devised the displacement current and hence the space and time variant displacement field $\mathbf{D}$

$$\mathbf{D}(r, t) = \varepsilon_0 \mathbf{E}(r, t) + \mathbf{P}(r, t) = \varepsilon_0 \varepsilon_r \mathbf{E}(r, t)$$

where $\mathbf{D}$ is the displacement field vector, $\mathbf{E}$ if the electric field and $\mathbf{P}$ is the polarization density vector. Maxwell’s equations then are able to provide an interface between the extreme domains through the dielectric constant by way of smooth shapes (spheres or ellipsoids of revolution), the mesoscopic cavity. For the optical range, this cavity had to be much smaller than the wavelength of light (hence, quasi-static, at the infinite wavelength limit). Details of quantum electronic nature are not required in this mode of treatment.

When modeling nanomaterial optical properties, certainly over the past several decades, optical constants $n$ (refractive index) and $k$ (extinction coefficient) were normally extracted from well-established data tables [16]. Data from Johnson & Christy’s famous work were obtained by measuring reflection and transmission in vacuum on evaporated thin films with thickness ranging from 20 to 50 nm [16]. These data, though excellent in providing approximate values, are held in question when directly applied to nanomaterials. Not only do optical constants differ according to method of surface preparation, for example, optical constants ($n$ and $k$) determined by ellipsometry on electroplated gold surfaces; but in addition, they are influenced by intrinsic (quantum) size effects [17]. Optical constants of gold nanoparticles embed within titania matrix were extracted by researchers using spectroscopic ellipsometry [18]. Their model was able to demonstrate anomalously high near-infrared absorption by such small nanoparticles, when optical constants from data tables were applied in simulations. Furthermore, semiconductor nanoparticles are expected to undergo optical bandgap variation upon diminishing size [19]. Semiconductor band gap energy $E_g$ expands as particle size is diminished leading to concomitant changes in refractive index and absorbtivity.

**Effective medium treatments**

Effective medium approximations or theories (EMT) are capable of describing macroscopic properties of composite materials based on proportional blending of optical or electronic properties of components [20]. They are considered to be self-consistent, phenomenologically based continuum averaging techniques. Therefore, EMTs provide approximations of composite material behavior that are based on the relative volume fractions of its components [21]. EMT’s are rooted within classical physics, in particular, classical electromagnetic theories. In the middle of the 19th century, Ottavio-Fabbrizio Mossotti (1850) developed the first form of the expression later to be modified by Rudolf Clausius (1879, the explicit form) to yield the well-known Clausius-Mossotti relationship – later to be embellished further by Ludvig Lorenz and Hendrik Lorentz (polarization leading to local field correction). The host medium was assumed to be vacuum or air in those expressions and mainly applicable for spherical particles or cavities. Today, numerical techniques based on discrete dipole approximations evolved from the
Clausius-Mossotti relationship. These EMT homogenization techniques were based on classical and macroscopic constitutive relations derived from Maxwell’s equations [22]. Modern theories of polarization address computations of induced microscopic currents in condensed media by application of density functional theory [22,23].

Two general forms of EMT are commonly used in simulations: the Maxwell-Garnett (1904) and the Bruggeman homogenization forms. In the former, volume fraction of the composite inclusion is expected to be small with respect to the host medium (usually a dielectric material). In the latter, volume fractions of inclusion and host are on par. The Maxwell-Garnett and Bruggeman are widely known and need not be displayed at this juncture.

We have used EMTs extensively in the past to model extrinsic size effects [24] however this simulation method is limited with regard to accurately quantifying intrinsic (quantum) size effects [7]. Extended effective medium theories try to incorporate size-dependent electromagnetic effects like dynamic depolarization, extinction and retardation effects. Mie scattering theory is best applied to homogeneous spherical particles. Extrinsic size effects are those governed by particle size, shape and orientation with respect to the wavelength of light [24]. In other words, the optical constants $n$ and $k$ (sequestered with the dielectric constant $\varepsilon$) input into classical EMT are simply those of the bulk material and are functions of the wavelength of the light, $\varepsilon = \varepsilon(\lambda)$ with $d > 10$ nm. Regarding intrinsic size effects, applicable to particles less than 10 nm radius, $\varepsilon = \varepsilon(\lambda, d)$, optical constants are expected to be a function of size as well [24].

**Maxwell-Garnett EMT and FEM**

Many years ago, we conducted simulations from programs that we generated in MATLAB and other platforms. However, our programs were limited to spherical or ellipsoidal shapes due to the necessity of maintaining continuity within Maxwell’s equations. Now with the adaptation of finite element methods, we can input equations as well as multiple and variable shape data directly into FEM programs (e.g. COMSOL Multiphysics with wave optics module). Here we show a simple example of facilitated simulations created by FEM. In Figure 1, absorption spectra of spherical to cylindrical gold nanoparticles embedded homogeneously within an isotropic porous alumina parallel channel matrix, calculated by dynamical Maxwell-Garnett approximation, are input into an FEM program [20,25]. Input parameters included length $a$ (varied from 20 to 100 nm), diameter $b$ (fixed at 20 nm), and volume fraction $f_i$ (fixed at 0.05). The orientation of the particle array (i.e. the pore channels in the alumina membrane) was held perpendicular to the electric field of the incident light. It is clear from the simulation shown in the figure that a blue shift in absorption occurs with increasing aspect ratio. Application from this kind of result can be useful in designing filters and waveguides and made facilitative by application of FEM to classical electromagnet equations.

**Bruggeman EMT and FEM for optical properties- a case study**

A wide variety of computational methods have been developed and implemented to simulate the properties of anti-reflective coatings [26]. Effective medium theory (EMT) [27], finite-difference time-domain (FDTD) [28], transfer matrix method (TMM), rigorous
coupled-wave analysis (RCWA) \cite{29,30} and the finite element method (FEM) \cite{31}, are commonly used for predicting the optical properties of solar cell applications for example. The OPTOS (optical properties of textured optical sheets) simulation formalism \cite{32–34}, recently developed by the Fraunhofer Institute, is a more advanced computational technique dedicated to simulating textured surfaces with low computational costs. Here we detail a simple method based on the well-known Bruggeman effective medium approximation to model randomly patterned nanostructured layers acting as anti-reflection coatings for a simple air/glass interface and make predictions for their optical properties. Figure 2 depicts examples such layer.

The characteristic length of the surface roughness, or equivalently the average distance between particles, $a$ is taken to be less than that of the wavelength of the electromagnetic radiation of interest. This condition is necessary for effective medium theories to apply. In this limit, the subwavelength nanostructures cannot be resolved by the electromagnetic waves: as the light traverses the nanolayer it will interact with the nanostructured layer as if it was a continuous stack of infinitely thin homogeneous sublayers, each of which being characterized by an effective refractive index. In other words, the nanolayer can be modelled as an inhomogeneous layer with a gradually varying refractive index (Figure 3). In this regime scattering is negligible.

The nanolayer acts as an impedance matching layer for the light. This gradual transition from a medium of low refractive index (the incident medium: air) to a medium of higher refractive index (the substrate: glass) reduces reflection losses through a series of destructive (constructive) interference of the waves being reflected (transmitted).

The representative unit elements of the nanolayers studied here are shown Figure 4. They are characterized by the following nanoparticles profiles that we define as: linear,
quadratic, and elliptical. The aspect ratio for each nanoasperity is fixed to 2. The particles are distributed randomly with an average separation $a$ (Figure 5).

To calculate the effective refractive indices, the Bruggeman formulation requires the knowledge of the dielectric functions of the nanoparticle material and the surrounding medium, a shape factor characterizing the aspect ratio and interaction of the particles.
with the field: the depolarization factor. It also requires the volume fraction $f$ of the material considered.

$$f_{\text{air}} \left( \frac{\varepsilon_{\text{air}} - \varepsilon}{\varepsilon_{\text{air}} + (P_i^{-1} - 1)\varepsilon} \right) + f_{\text{SiO}_2} \left( \frac{\varepsilon_{\text{SiO}_2} - \varepsilon}{\varepsilon_{\text{SiO}_2} + (P_i^{-1} - 1)\varepsilon} \right) = 0$$

where $f_{\text{air}}$ and $f_{\text{SiO}_2}$ are the volume fractions of air and silica respectively, $\varepsilon_{\text{air}}$ and $\varepsilon_{\text{SiO}_2}$ their dielectric functions, $P_i$ are the depolarisation factors and $\varepsilon$ the effective dielectric function from which we will obtain the effective refractive index $n$ using $n = \sqrt{\varepsilon}$, as none of the materials considered here absorb or exhibit magnetic properties.

Here, the volume fraction for each particle profile is a function of the height $h$ and can be calculated by simple geometrical considerations (Figure 6). Since the nanoparticles have cylindrical symmetry we can define the functions $r_l$, $r_q$, and $r_e$ describing the height-dependent cross-sectional radii for the linear, quadratic and elliptical profile cases respectively:

$$r_l(h) = \frac{a}{2} \left( 1 - \frac{h}{a} \right)$$

$$r_q(h) = \frac{a}{2} \left( 1 - \left( \frac{h}{a} \right)^2 \right)$$

$$r_e(h) = \frac{a}{2} \sqrt{1 - \left( \frac{h}{a} \right)^2}$$

For an infinitesimal slice of height $dh$ the volume of material at height $h$ is then $\pi (r_i(h))^2 dh$, and the corresponding total volume of material and air is $(2r_i(0))^2 dh$, so that the height-dependent volume fractions are then given by: $f_i(h) = \pi (r_i(h)/2r_i(0))^2$ with $i = l, q, e$.  

Figure 5. Dimensions corresponding to the linear (a), quadratic (b), and elliptical (c) profiles.
Together with the refractive index of the base material considered, the functions $f$ are the only parameters that determine the anti-reflective properties of the layer.

We will approximate the modelling of the surface by decomposing the nanolayer using only a finite number of sublayers, instead of a continuum (see Figure 7). This assumes that the volume fraction of silica can be considered to decrease in a stepwise manner as a function of height. To simplify the calculation of the depolarization factors, at each sublayer we will also assume that the geometry of the material (e.g. a truncated cone for the linear profile case) can be replaced by a sphere with equivalent volume fraction. The depolarisation factors $P_i$ of a sphere are all equal to $1/3$, we then obtain the following simplified Bruggeman expression:

$$f_{\text{air}} \left( \frac{1 - \epsilon}{1 + 2\epsilon} \right) + f_{\text{SiO}_2} \left( \frac{\epsilon_{\text{SiO}_2} - \epsilon}{\epsilon_{\text{SiO}_2} + 2\epsilon} \right) = 0$$

The resulting height-dependent refractive indices are shown Figure 7. The gradient in refractive index, between the air/glass interface, although discontinuous, typically allows for a higher transmission of light, as will be discussed below.

To simulate the optical properties of the substrate/sublayers system, the Fresnel equations may be used in combination with a transfer matrix method [35]. Another method is to input the model into a FEM package, such as COMSOL and to solve for the transmitted and reflected fields using Maxwell’s wave equation. As a general requirement for EM FEM calculations, a fine enough meshing ($<\lambda/10$) should be used as well as a large enough computational domain ($\approx \lambda$) (Figure 8) so that numerical artefacts such as unwanted boundary reflections can be avoided. In our FEM simulation, the incidence of

Figure 6. The calculated volume fractions for the linear (a), quadratic (b), and elliptical (c) profiles as a function of layer height. The continuous curves are approximated by a discontinuous gradient, composed of 4 steps of equal height: each step represent the layers used to simulate the ARCs.

Figure 7. The calculated effective refractive indices for the linear (a), quadratic (b), and elliptical (c) profiles as a function of layer height, for a wavelength of 650 nm.
the electromagnetic field is kept normal to the surface. The total height of the sublayer stack has been set at 400 nm, bearing in mind that for the visible part of the solar spectrum as a light source, the accuracy of the model is higher for longer wavelengths.

The refractive index gradient allows to minimize reflectance losses for all 3 profiles as compared to bare glass (Figure 9). The fashion in which the mixture of air with silica is increased from substrate to air has a strong impact on overall reflectivity. Numerical and experimental studies of multilayer graded-index profile have shown that a quintic or 5th order polynomial profile for the refractive index results in optimum anti-reflective properties [36–38]. In the present case however, the relative performance of the modelled layers seems to follow the refractive index contrast at the first sublayer/air interface. The elliptical profile model results in a more severe contrast in which case we would expect, as is the case, a higher proportion of light being reflected. For the quadratic profile, as the first step presents a smoother transition into the medium, lower reflectivity is obtained. This effect is also accompanied by less interference patterns (oscillations in the reflectance spectra due to Fresnel reflections). The linear case presents the softest transition for the light, from air to medium, and results in no interference pattern and a transmission enhancement > 4% across a wide bandwidth of the spectrum.

Figure 8. FEM simulation domain.
Multiscale theoretical frameworks

Material simulation overview

Simulations of nanomaterials’ optical response essentially follows historical development of computational materials sciences, starting with classical Maxwellian electrodynamics and Lorentz oscillator model, through more refined semi-classical approaches. Including both wave function and electron density-based approaches, they can provide dielectric function beyond Drude approximation, through various homogenization models, culminating with fully atomistic quantum methods. The hierarchy of state-of-the-art modeling approaches therefore retains this historical development with full-wave classical electrodynamics modeling, applicable to nanoparticles and nanostructured materials on top, fully atomistic time-dependent methodologies for calculating optical properties of small clusters at the bottom, with the development of dielectric function beyond classical electrodynamics approaches in-between (Figure 10). The ultimate goal is to develop a multi-scale theoretical framework that integrates phenomenological models describing the essential physics of light-matter interactions with full-wave electromagnetic analysis and comprehensive microscopic modeling.

To analyze optical properties of materials of interest one has to transform information obtained at the quantum level to relevant macroscopic properties for using with the Maxwellian constitutive relations. In general, three different tiers of theoretical modeling can be applied to undertake this non-trivial task: (i) modeling of intermolecular interactions and their influence on the property; (ii) linear scaling methodology, and (iii) multiscale modeling. The first approach involves models based on reaction field theory and polarizable continuum methods. Linear scaling is more elaborate method in which rigorous quantum mechanics is transcended by successive enlargements of the molecular models (the number of atoms) until the property value is converged. Ideally linear scaling methods can be implemented to be proportional to the system size, thereby extending the applicability range into the nanoscale regime, beyond ten thousand atoms. This is not achieved merely through high-performance computing, but rests...
critically on the development and adaptation of new computational schemes. Another, conceptually different approach to close the gaps between micro- and macro-scales is offered by multiscale modeling technology. The most important variation of contemporary multiscale modeling from atomic size elements to macroscopic homogenous media is given by the combination of quantum mechanics and extended classical physics models. This theoretical framework endows various models with rigorous insights extracted from the quantum nature of materials at the atomic scale and builds them into equations that are solved by advanced numerical techniques. In particular, joining quantum mechanics (QM) with molecular mechanics (MM) has become an important and popular area in 'in silico' research across a wide variety of fields (QM/MM). The multiscale modeling paradigm is sketched in Figure 11.

The calculations of optical properties at the quantum level have extensively utilized the analytical response theory [39]. Within the response theory paradigm, excitation energies and excited state properties are generated by applying time-dependent perturbation theory, but without explicitly solving the Schrödinger equation for each excited state. Response functions can be obtained with either the Ehrenfest method or quasi-energy method [40]. Thus, polarizability tensors are computed directly for given frequencies without approximations other than those, dictated by the computational model. The formalism is completely generic with respect to the source of the perturbing fields (external or internal) and type of field (electric, magnetic or mixed), and time dependence (time-dependent or time-independent fields). The response theory yields

![Figure 10. Hierarchy of systems and modeling methods.](image-url)
the real and imaginary parts of molecular polarizabilities directly as a function of the excitation frequencies without recourse to sum-over-states (SOS) formulation. One critical extension of the response theory is the complex polarization propagator approach \[41\], which is a resonant convergent response theory that accommodates resonant properties.

An example of using fully atomistic description is ultra-small metal nanoparticles (clusters). Such noble metal clusters can maximize direct enhancement of optical properties of bound molecules while minimizing losses, inherent to larger size noble metal nanoparticles. In fact, small size clusters do not support plasmon resonance. Thus, optical losses associated with plasmon resonances are not an issue. For the smallest particles, which range from well-defined clusters of 4, 11, 20, 25 or 38 gold atoms \[42–45\] to a few hundred atoms, both the absorption and field enhancement become increasingly sensitive to the environment, and the concept of field enhancement based on plasmonic behavior and the Drude model breaks down. Fully atomistic description of gold atoms requires incorporation of relativistic effects into the calculation, which can be done at the minimal cost with the use of effective core pseudopotentials \[46\].

One recent extension of the hybrid QM/MM approach is a capacitance-polarization force field, used for simulating the optical response of metal nanostructures in complex environments \[10\]. To date, such multiscale integrated approaches have mostly been applied to fully organic systems, while organometallics, or systems incorporating nanoparticles with free charge carriers, have received relatively less attention. However, nanoparticle-enhanced materials show unique capabilities for a wide range of applications in sensing, imaging, molecular electronics and energy conversion – within or outside of the plasmonic regime. An obvious complication of metallic particle embedding is the almost free motion of charges within the metallic cluster, and that the
interaction with the QM shell should be regulated by ‘atomic capacitances’ rather than by fixed charges in addition to polarizabilities. The so-called quantum mechanics/capacitance molecular mechanics (QM/CMM) model provides a practical approach for theoretical modeling of optical properties of molecular moieties interacting with inorganic surfaces [47,48]. Here, the heterogeneous MM part is split into metallic and non-metallic parts, assuming a capacitance-polarization model for the electrostatics and polarization of the metallic part (resistance and inductance) and distributed charges for the non-metallic part. The implementation of a heterogeneous MM region captures the essential physical features of a material containing metal nanoparticles and molecules interacting with them.

Several obstacles have yet to be overcome to reach the full capacity of the QM/CMM method. When coupled to the response theory, it can effectively model the full spectrum of properties of hybrid inorganic-organic nanocomposites. However, the homogenization of force fields used in the dynamics and property parts of the calculations over the entire system represents a substantial challenge. The bond capping, charge balance and treatment of short range interaction and charge transfer between the QM and MM systems are notoriously challenging issues. Recent developments of computational methods and techniques are targeting these challenges. For example, fully atomistic treatment of plasmonic nanoparticles has become a reality thanks to novel algorithms and increased computing power [49].

On the other end of the spectrum, the full-wave classical electrodynamics algorithms use both differential and integral equation based methods and acceleration approaches, to predict the high-frequency electromagnetic response of nano- and mesoscale materials [50–58]. In particular, the finite difference frequency domain (FDFD), finite element analysis (FEA), discrete dipole approximation (DDA), and extended beam propagation methods (BPM) that incorporate forward- and backward-propagation effects can be used to compute key measurable quantities such as transmittance and reflectance spectra. Many of them are integrated into state-of-the-art commercial software packages (e.g. COMSOL [59]). Many of these packages allow for custom modifications comprising extended dynamical equations that describe quantum aspects of nanoscale material behavior.

Refining the dielectric function of plasmonic materials, particularly emerging and alternative materials, beyond the limits of conventional classical electrodynamics-based models, bridges quantum and classical approaches and allows to obtain fundamental new knowledge of material responses at the nanoscale. Over the decades, technological progress has led to a steady miniaturization that has resulted in features with near-atomic size. However, for the classical dielectric function to remain a valid concept, the size of the cluster/particle should be sufficiently large, larger than the mean-free path of charge carriers. Classical electrodynamics is based on averaging process that turns the rapidly fluctuating microscopic fields found near individual atoms into macroscopic fields averaged over a volume of space that may contain myriad of such atoms, or dipoles, so much so that the medium loses its granularity and becomes a continuum, necessitating only the mere application of boundary conditions [60]. Obviously, this simplified picture fails if the macroscopic theory is applied to systems with features that are only a few atomic diameters in size. This is already the case for typical nanowire and/or nanoparticle systems that are now easily fabricated with features so small and so closely spaced that the electronic wave functions
spilling outside their respective surfaces may begin to overlap. The diameter of a typical noble metal atom is approximately 3 Å, while the electronic cloud forming at and shielding a flat, noble metal surface may extend several Angstroms into free space. The linear optical response of metals in classical electrodynamics is almost exclusively modeled under the assumption that a metal (especially a noble one) can be represented by the ionic core surrounded by a cloud of free electrons that is driven by an incident electric field. The resulting dielectric response depends only on the frequency of the incoming light. However, this model is inadequate to describe experimental observations. It has been enhanced by hydrodynamic models that incorporate nonlocal effects, through terms like electron pressure \([61–66]\) and surface and bulk nonlinearities \([67–70]\). Ultimately the sub-nanometer gap between metals enables quantum tunneling \([-41,71–79]\), which also is incorporated into the dynamical models \([74]\).

Finally, effective medium analysis or homogenization can be further applied to obtain effective frequency-dependent bulk dielectric function that can be used for larger scale (macroscopic) material, device, and systems design. The effective medium analysis can identify optimum attributes of constituents such as size, spacing, ordering, and orientation that best enhances the target property. Here, the basic quantum description of electronic structure can be combined with nonlinear Maxwell’s equations and the density matrix approach. In this way one obtains not only a connection to field interaction with the macro-structure of the bulk material, but also how the ingoing fields transform to local fields, which is crucial to properly assess experimental results. Effective medium theories such as the Maxwell-Garnett approach are of great use here to obtain macroscopic bulk effective parameters of a composite material from its microscopic characteristics.

It has to be mentioned that traditional plasmonic materials, such as gold and silver (less so platinum and aluminum) have long been the ‘golden’ standard for applications utilizing the operation wavelengths falling into the visible range. However, it has been realized that the intrinsic lossyness of these materials impedes their application in the emerging fields such as metaphotonics \([80]\). Recently, alternative low-loss plasmonic materials have emerged such as titanium nitride (TiN), indium tin oxide (ITO), Al:ZnO (AZO), In:CdO, B-hyperdoped Si, and copper chalcogenides \([81]\). They allow for tunable local field enhancement in the short wave infrared region (SWIR). These materials generally exhibit a smaller imaginary contribution to the dielectric function than noble metals, especially in the IR range. Modeling of the alternative materials and devices based on them adheres to the strategies outlined above.

**Practical applications of simulations**

**Anti-reflection coatings**

We return to discussions about anti-reflection coatings (ARCs). Anti-reflection coatings are technologically important subwavelength structures, that are also found naturally. The eyes of 19 diurnal butterfly species were analyzed by Stavenga *et al.* \([82]\) and reported to have arrays of periodical conical structures each having height about 230 nm acting as perfect anti-reflecting layer providing protection from predators. Today several nanostructures with variety of shapes have been produced artificially to
explore their application as ARC in many areas, such as solar cells, optical lenses, automobiles etc [83,84]. Optical modelling methods have developed rapidly in recent times with advanced computational ability and has been applied widely for ARC design. Amongst numerous modelling methods, finite element method (FEM), finite-difference-time-domain (FDTD), transfer matrix method (TMM) and rigorous coupled-wave analysis or Fourier modal method (RCWA/FMM) are the commonly used methods in the field of optical modelling for ARC [85]. Effective medium theory (EMT) is another method widely used for determining the effective index of refraction of the subwavelength ARC structures [86]. But EMT is limited to structures much smaller (typically one tenth) of the light wavelengths [87], and hence needs to be considered carefully.

Several researchers have used FDTD methods for optical modelling of ARC, mostly when considering ARC based on optically thin dielectric materials. Lesina et al. [88] has reported design of ARC for silicon solar cells based on plasmonic silver (Ag) nanoparticles with silica overlayer. Using FDTD methods they have investigated the effect of nanoparticle size, their location within the ARC layer and surface coverage on the ARC performance. Feng et al. [89] has compared FDTD method with TMM method for multiple thin film based ARC and reported that FDTD methods have better accuracy than TMM. Similar comparisons have been reported by other researchers as well [90,91] showing FDTD with higher accuracy over TMM methods. However, FDTD methods are more time consuming compared to TMM methods.

Unlike FDTD method, which is a time domain optical modeling method, FEM is a frequency-based optical modeling method also reported widely for ARC modelling. High accuracy and use of boundary conditions reducing the unwanted edge reflection are some of the advantages of FEM [92,93]. FEM is also capable of multiphysics modelling. Lee et al. [94] has reported a 2D FEM simulation for silicon nitride (Si$_3$N$_4$) as ARC and examined the geometry-dependent effective reflectance of the Si$_3$N$_4$ sub-wavelength structure over the wavelength ranging from 400 nm to 1000 nm. Using optimum conditions for Si$_3$N$_4$ ARC layer they have calculated almost 1% enhancement in the efficiency of a P-N junction solar cell. Geometry and arrangement of sub-wavelength ARC structures are also investigated by Hishikawa et al. [95] using FEM modelling and showed randomly arranged triangular pyramids are more effective as ARC.

Similarly, other frequency-based optical models, such as RCWA and TMM, has been used to investigate a wide range of ARC materials. A variety of geometries including moth-eye like conical arrays, inverted moth-eye structures, hexagonal closed-packed, tapered and truncated cones, nanopillars, and core/shell structures have been evaluated by using RCWA methods [96–99]. TMM method is used for layered thin films and employs continuous boundary conditions for reflectance estimation. Combination of TMM and EMT was used by Forberich et al. [100] to calculate optical absorptions in solar cells with ARC based on moth-eye structure. The reflectance profile of the ARC layer was evaluated by EMT, while TMM was used to simulate the optical absorptions of the solar cells. A seven-layer ARC for solar cells with 1% – 6% reduction in reflectance was reported by Kuo et al. [101], where TMM was used to model the reflectance of the layered ARC.
**Optical filters**

Optical filters are devices which allow transmission of selective wavelengths based on their design. They are commonly used in various optical and opto-electronic devices. FDTD simulation was used by Hosseini *et al.* [102] for the design of a low pass optical filter based on a plasmonic nanostrip waveguide capable of proving sub-wavelength confinement. The simulated filter showed flat low pass filter with 3 dB attenuation at the optical communication wavelength (\( \lambda = 1.55 \text{ µm} \)). Another FDTD simulation was reported by Lee *et al.* [103] for simulating transmission characteristics of transparent conducting electrodes composed of silver or aluminum grids with widths from 25 nm to 5 µm.

A high performance bandpass filter using single-layer resonant Si gratings was reported recently, where filter transmittance was simulated by using FEM method [104]. A narrowband tunable antireflection optical filter was reported by Bibbo *et al.* [105] where the filter is composed of three layers with a metasurface consisting plasmonic nanoparticles. FEM simulation was used for the parameters of the materials used in the filter design and to estimate the refractive index of the layers. The simulation also showed that the resonance peak of the plasmonic layer can be tuned by controlling the refractive index of the dielectric layer. A LiNbO\(_3\) layer was considered as the dielectric layer in this case. In another work, FEM was used for modelling diffraction grating based optical filters for fluorescence detection of biomolecules. Authors have evaluated three filter concepts using the FEM modelling [106], namely placement of the diffraction grating, embedded diffraction grating in a low refractive index medium and combination with a flat absorbing filter. The first one showed minimal improvements in terms of filter efficiency, while the other to produces high efficiencies (in the order of \(10^5\)).

**Solar cells**

Optical simulations for solar cell design are becoming very common these days. Such simulations help researchers to save time and predict the characteristics of the device ahead of the actual experiments. To improve solar cell performance one of the common approaches is to employ antireflection coatings on solar cell surface to increase optical transmission. Optical simulations related to antireflection coatings have been discussed earlier. Another approach to improve solar cell efficiency is by light trapping within the cell to maximize the optical absorption resulting in more photocurrent. Several strategies have been reported for light trapping purpose that can be very useful for solar cell applications [107]. Light trapping by periodically textured surface with realistic interface morphologies for amorphous silicon solar cell was investigated by Jovanov *et al.* [108]. A similar micro-textured light trapping layer was reported for thin film organic solar cells [109]. In both the cases FEM simulation was carried out to evaluate the light trapping behavior of such textured layers and their impact on the solar cell output. More than 60% of less optical reflection due to the light trapping was predicted from the simulation resulting in almost 20% improvement in the short-circuit current of the cell. A nanostructured grating was proposed as a light trapping method for solar cells by Das *et al.* [110]. Using FDTD methods authors have calculated about 2% reduction in the reflection when a triangular shaped nanostructured grating with height of about 300 nm
and the period of about 830 nm was used. This value of reflectance is almost 28% lower than the flat type substrates.

RCWA modelling have been also widely used for optical simulation of solar cells [111–113]. RCWA modelling provides high accuracy, while FEM and FDTD are time and CPU consuming approaches with advantages of multiphysics modelling. Apart from light trapping, several simulations are done on the structure of the solar cell materials aiming for high efficiency. Si nanowire (NW) based solar cells have been extensively investigated by Foldyna et al. [114,115] using RCWA modelling approach. With increasing NW length from 1 to 10 μm, they have demonstrated improvement in short circuit current density from 25 mA/cm² to 34 mA/cm². The optical absorption profile of these Si NW was investigated by Lin et al. [116] by using TMM method. From the calculations, they have proposed an optimum dimension for the Si NWs with diameter 540 nm and periodicity 600 nm. Using these optimum conditions almost 70% enhancement in the efficiency of the Si NW solar cell was finally predicted.

‘Post scriptum mechanicus’ and looking forward

We have focused heavily on optical aspects in this paper but must not neglect other aspects of physical properties – those areas arising from civil engineering, mechanics and now, nanomechanics. The finite element treatment, as allude to earlier primarily to solve engineering problems. It originated in the 1940’s by A. Hrennikoff and R. Courant [117,118]. By the early 1960’s, Feng Kang of China and western researchers developed a numerical method to solve partial differential equations called the finite difference method based upon the variational principle – better known as the finite element method (FEM). In the 1980’s Feng Kang integrated dynamical systems like the Hamiltonian and wave systems into analytical techniques. The FEM is considered to be a landmark of computational mathematics. This segue is provided to link

Nanomechanics

Average property determination requires spatial averaging. Consequently, regarding the non-local, where the stress at a point cannot be determined alone from the strain at that point, constitutive relations emerge [119]. The resulting stochastic differential equations for equilibrium demands advanced formulations [120]. The spatially discretized finite and boundary element models necessitate stochastic shape functions and stochastic Green’s functions, respectively [121,122]. Symbolic methods become indispensable for carrying out operations of lengthy algebraic expressions [123]. Nanomechanics must utilize the most accurate computational schemes. Conventional commercial packages provide a number of finite element solvers that fail to address the effects of Poisson’s ratio and especially incompressibility [124,125]. The response computation for stochastic nanomechanics formulations calls for computation intensive Monte Carlo simulations. Therein considerable economy can be achieved by ordering the Monte Carlo samples and carrying out an incremental strategy in the sample space [126].
Mechanics modeling with FEM

Finite element analysis has been accomplished recently in describing the performance of a cantilever mechanical energy harvester based on nanoscale layer of zinc oxide (ZnO) piezoelectric nanomaterial [127]. The purpose of the simulation was to show the feasibility of applying an energy harvester that is able to detect low frequency vibrations under ambient conditions (for example, flowing fluid within a pipe). The link of the device was to a wireless sensor node system. Application of COMSOL Multiphysics, for example, was able to simulate resonant frequency modes at selected frequencies. The images below depict input parameters and simulations at various frequencies (Figure 12).

Simulation of the cantilever at three eigen-frequency modes are shown in Figure 13. The eigen-frequencies obtained were 575.5, 1810.6 and 3957.3 Hz. Since the energy harvester is based on the lowest frequency, that frequency was considered to be the fundamental frequency. The maximum voltage output obtained (by simulation) was 0.32 V at 575.5 Hz input (Figure 14). This is due to the impact of a piezoelectric zinc oxide layer, considered to be deposited at the microcantilever surface, which is subjected to large deflection at the resonance frequency.

Conclusions

We have presented a brief overview of progress in nanomaterial design theory and simulation. Coupled classical electromagnetic theory with finite element methods have shown facilitative simulation capability in designing anti-reflection coatings – especially with regard to modeling of coatings that consist of layers made of nanoparticles of complex shape. With the advent of ever more powerful open source or commercially available programming packages and new and more powerful computational methods, such as those of Materials Studio™ [128], nanomaterial modeling will gain in popularity and be available to more researchers. There are ingenious ways to create hybrid methods that link Schrödinger’s equation with Maxwell’s equations and continuing on to the macroscopic level. An all-encompassing unified method is still off into the future however enough technology is available to accurately model nanomaterial physical properties, especially those of optical properties. Ironically, it will be, we predict, by
quantum computing that quantum mechanics is utilized to completely characterize material behavior, at the least for mesoscopic systems.

Figure 13. Top left: First-mode resonant frequency at 575.5 Hz. Top right: Second-mode resonant frequency at 1810.6 Hz. Bottom left: Third-mode resonant frequency at 3957.3 Hz.

Figure 14. Voltage vs. frequency of the potential energy harvester as simulated by COMSOL Multiphysics program. The maximum voltage was derived from the resonant frequency at 575.5 Hz.
Disclosure statement

No potential conflict of interest was reported by the authors.

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