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Multiscale modeling and computation of optically manipulated nano devices

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ABSTRACT

We present a multiscale modeling and computational scheme for optical-mechanical responses of nanostructures. The multi-physical nature of the problem is a result of the interaction between the electromagnetic (EM) field, the molecular motion, and the electronic excitation. To balance accuracy and complexity, we adopt the semi-classical approach that the EM field is described classically by the Maxwell equations, and the charged particles follow the Schrödinger equations quantum mechanically. To overcome the numerical challenge of solving the high dimensional multi-component many-body Schrödinger equations, we further simplify the model with the Ehrenfest molecular dynamics to determine the motion of the nuclei, and use the Time-Dependent Current Density Functional Theory (TD-CDFT) to calculate the excitation of the electrons. This leads to a system of coupled equations that computes the electromagnetic field, the nuclear positions, and the electronic current and charge densities simultaneously. In the regime of linear responses, the resonant frequencies initiating the out-of-equilibrium optical-mechanical responses can be formulated as an eigenvalue problem. A self-consistent multiscale method is designed to deal with the well separated space scales. The isomerization of azobenzene is presented as a numerical example.

1. Introduction

Optically manipulated nano devices have attracted a lot of recent interest with applications in solar energy harvesting, molecular engineering, molecular sensing and non-invasive regulation of intra-cellular reactions [12,16,30,29]. One such example is a photoresponsive DNA nanomotor enhanced by silver nanowires as illustrated in [30]. Illuminated by ultraviolet (UV) and visible lights, the nanomotor can switch back and forth between 'open' and 'loop' states, thereby converting photonic energy to mechanical energy. The mechanism is facilitated by incorporating azobenzene moieties that can change conformational structure through the *cis–trans* isomerization. The efficiency of the conversion can be significantly enhanced by a plasmonic near-field coupling with silver nanoparticles, due to the spectral overlap between the azobenzene absorption

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band and plasmonic resonances of silver nanowires. Recent applications include photon regulated enzymatic nanostructures, drug releasing from nanocontainers, mRNA detection in living cells, etc. A quantitative investigation of this type of nano scale optical-mechanical systems will obviously help to find optimal designing and novel applications.

From the modeling point of view, when the system is of nano scale, the macroscopic theory for the electromagnetic (EM) field fails to capture the microscopic and nonlocal character of the light–matter interactions, which suggests the quantum mechanical description of the current and charge densities. Quantum Electrodynamics (QED) [7] gives a complete description of the interactions between the EM field and the charged particles, but has limited applications to complex systems due to its high computational expenses. Semi-classical theories [23,17,6] combine the classical treatment of the EM field and the first principle approach to the charged particles. Different from QED, in a semi-classical theory, the EM field is not quantized, therefore lower computational cost is required. The EM field as well as the current and charge densities are determined self-consistently through coupled Maxwell and Schrödinger equations. However semi-classical theories are still prohibitively expensive for most applications of interest in nano optics since the high dimensional many-body Schrödinger equations still need to be numerically solved.

In a previous paper [2], we incorporated Time-Dependent Current Density Functional Theory (TD-CDFT) [14,22,11] into the framework of the semi-classical optical response theory, thereby avoiding the computational cost of solving the Schrödinger equation. In the Density Functional Theory (DFT) for the ground state of electrons, a one-to-one correspondence up to an arbitrary constant between the external potential and the ground state electron density has been established in the seminal work of Hohenberg and Kohn [14]. Hence, the wavefunction can be obtained as a functional of the electron density, which allows the evaluation of all observables of the system. Similar results have been extended to the case of time evolutionary electronic structures in the form of Time-Dependent Density Functional Theory (TD-DFT) by Runge and Gross [22], and later to the situation of external electric and magnetic fields with arbitrary time dependence by Ghosh and Dhara [11] in the form of TD-CDFT, where the current density is introduced as the fundamental variable. A practical Kohn–Sham (KS) system [18], which is a numerically tractable single-particle system under effective external potentials, was introduced to compute the electron and current densities such that they are the same as those in the original interacting system under consideration.

We call the system obtained in [2] the Density Functional semi-classical theory for nano-optics, which is a combination of the semi-classical theory with TD-CDFT and can be formulated as coupled Maxwell–Kohn–Sham (Maxwell–KS) equations (also see [3,19,8]). In the regime of linear responses, a system of linear equations for concurrently determining the EM field, the current density and the electron density can be derived. Moreover, the zero eigenvalue problem of the linear system corresponds to the resonant eigenmodes [6] of the nano-optical response. To deal with the disparate space scales of the system, we proposed a multiscale scheme which can solve the system self-consistently by allowing communications between the macro-solver for Maxwell equations and the micro-solver for Kohn–Sham equations. Numerical experiments with simple molecular structures such as methane have shown validity of the model as well as efficiency and accuracy of the scheme.

In this work, we study the light driven nano devices by further introducing the molecular motion into the system through the Ehrenfest molecular dynamics [21], where the excitation of the electrons and the motion of the nuclei are separated under the single-determinant approximation and molecular dynamics is obtained by the mean-field approximation [24]. The coupled system of classical electromagnetism and Ehrenfest molecular dynamics along with TD-CDFT, which we refer as the Maxwell–Ehrenfest–Kohn–Sham equations, provides a computationally practical model to investigate the optically manipulated nanostructures. Within the linear response regime, we formulate a linear system that determines the induced EM field, nuclear positions, and current and charge densities simultaneously. Similar to [2], we can determine the resonant conditions initiating the molecular motion by solving an eigenvalue problem. The multiscale scheme introduced in [2] will also be generalized to deal with the three level system with well-separated electromagnetic, molecular and electronic scales.

The rest of the paper is organized as follows. In Section 2, we first incorporate Ehrenfest molecular dynamics into the Density Functional semi-classical Theory. Then in Section 3, we present the linear response formulation for the coupled Maxwell–Ehrenfest–Kohn–Sham system. The multiscale solver for the linear system is described in detail in Section 4. Finally in Section 5, azobenzene isomerization [13] will be presented as numerical examples. Throughout the paper, we will represent vector variables in boldface notations and scalar variables in the normal font.

2. The Maxwell–Ehrenfest–Kohn–Sham model

We first briefly review the semi-classical theory for nano scale light–matter interactions, the Ehrenfest dynamics and TD-CDFT separately, then formulate the Maxwell–Ehrenfest–Kohn–Sham equation by coupling these theories.

2.1. Semi-classical theory

In the semi-classical theory [6], the evolution of the EM field is determined by Maxwell equations in terms of the vector and scalar potentials $\{\mathbf{A}, \phi\}$ under the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$ with the following form: