Journal of Computational Physics 265 (2014) 145–155

Contents lists available at ScienceDirect

Journal of Computational Physics

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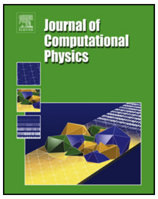

# Massively-parallel electron dynamics calculations in real-time and real-space: Toward applications to nanostructures of more than ten-nanometers in size

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ARTICLE INFO

*Article history:*
Received 17 November 2013
Received in revised form 30 January 2014
Accepted 4 February 2014
Available online 12 February 2014

*Keywords:*
Time-dependent density functional theory
Electron dynamics in nanostructures
Grid-based finite difference method
Massive parallelization

ABSTRACT

A highly efficient program of massively parallel calculations for electron dynamics has been developed in an effort to apply the method to optical response of nanostructures of more than ten-nanometers in size. The approach is based on time-dependent density functional theory calculations in real-time and real-space. The computational code is implemented by using simple algorithms with a finite-difference method in space derivative and Taylor expansion in time-propagation. Since the computational program is free from the algorithms of eigenvalue problems and fast-Fourier-transformation, which are usually implemented in conventional quantum chemistry or band structure calculations, it is highly suitable for massively parallel calculations. Benchmark calculations using the K computer at RIKEN demonstrate that the parallel efficiency of the program is very high on more than 60 000 CPU cores. The method is applied to optical response of arrays of $C_{60}$ orderly nanostructures of more than 10 nm in size. The computed absorption spectrum is in good agreement with the experimental observation.

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## 1. Introduction

Artificially designed nanostructures in response to light are promising materials for next-generation devices with valuable functions. For example, plasmon waveguides constructed from arrays of nanoparticles are expected to serve as photonic devices of energy and quantum data transfer [1]. Nanoparticles are structurally and chemically designed to work as highly efficient photocatalyst or sensitive chemical and biological sensors [2]. To develop these light-induced functional materials, understanding optical response, more specifically electron dynamics in nanostructures is essential. Nanostructures with the size of tens to several tens of nanometers are expected to provide unusual functions due to quantum mechanical finite-size effects differently from isolated or bulk systems.

Despite this importance, it is highly computationally demanding as matters stand to carry out photoinduced electron dynamics simulations even in nanostructures with the size of several nanometers. Excited state properties of molecules are calculated with chemical accuracy by using highly developed quantum chemistry (QC) approaches called post-Hartree–Fock methods [3]. Unfortunately, applications of such fairly accurate approaches are still limited to very small molecular systems and thus it is practically impossible to carry out those QC calculations of nanostructures with the size of 1 nm or more. Instead, as the first-principles calculations for materials relatively larger in size, Kohn–Sham (KS) density functional theory

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http://dx.doi.org/10.1016/j.jcp.2014.02.006
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(DFT) calculations have so far been preferably used as a standard QC or band structure (BS) approach because of the trade-off between computational costs and reliability [4–6]. Both methods indeed theoretically predict various kinds of physical or chemical properties of materials. However, since a set of analytic basis functions of atomic orbitals or plane waves is usually utilized in these computational methods, the costs of their computations are extremely high with increasing the size of a target system or a unit cell. This situation becomes much more severe particularly when calculating excited properties of systems. It is almost impossible in fact to calculate the optical response of nanostructures of more than ten nanometers in size. Furthermore, the conventional QC and BS methods invoking such a basis set expansion approach are not necessarily suitable for describing time-dependent phenomena in response to an external field.

An alternative method is a finite-difference (FD) approach in which a KS-DFT equation is directly solved on real space grids without invoking a basis set expansion. Thus, there is no computational procedure of solving eigenvalue problems or fast-Fourier-transformation (FFT), which are usually implemented in the conventional QC or BS calculations. This is a great advantage of the grid-based FD approach when conducting massively parallel calculations. Although the grid-based FD approach has a long history in the context of solving the Schrödingier equation of simple atomic systems, for example a hydrogen atom system [7], Chelikowsky et al. developed a practically useful high-oder-FD/DFT approach reliably applied to materials in combination with a pseudopotential method [8,9]. For the last two decade since then, the FD approach has been extensively used in calculating electronic structures and also optical response of materials [10–15]. In comparison with the conventional basis set expansion methods, the FD approach generally requires much more size of memory and is time-consuming to obtain converged results because the approach is based on a very simple and direct numerical algorithm. The FD approach is indeed less effective for calculating electronic properties of small molecular systems by utilizing a computer with a single processor or a relatively small number of multi-processors. However, the simple and direct FD algorithm overwhelms the parallel efficiency of the diagonalization or FFT procedures implemented in the conventional QC and BS calculations when carrying out massively parallel computations of large scale systems. We should also mention that self-consistent-field computations using Chebyshev-filtered subspace iteration were proposed in combination with an FD/DFT approach in real-space [16,17]. In this method, a nonlinear Chebyshev-filtered subspace iteration was adopted to avoid solving an eigenvalue problem except at the first self-consistent-field (SCF) iteration. The method with parallel computations is expected to be a powerful approach alternative to the conventional QC and BS calculations involving computationally demanding the SCF iterations.

We here develop a highly efficient grid-based FD computational program of electron dynamics in real-time and real-space in an effort to apply the method to optical response of nanostructures at a ten-nanometer scale or more. This is a core program of “Grid-based Coupled Electron and Electromagnetic field Dynamics (GCEED)” that is currently being developing in our proposed K computer project. The present computational approach is based on the time-dependent (TD) KS equation. We aim to develop a numerical program suitable for massively parallel computations in order to efficiently utilize the K computer at RIKEN. The TDKS equation is numerically solved in a direct manner at three-dimensional Cartesian grid points by employing an FD formula and the time-propagation is evaluated by the Taylor expansion method. Hybrid parallelization, MPI and OpenMP, is adopted. Computational efficiency of the method is demonstrated by calculating the optical response of arrays of $C_{60}$ with a size of 10 nm and more as sample systems.

Theory is described in the next section. Computational algorithms are described in Section 3. The details of the nanostructures considered are presented in Section 4. The massive parallelizations and their computational performance are discussed in Section 5 followed by the computational applications to $C_{60}$ nanostructures in Section 6. Discussion and conclusions are given in Section 7.

## 2. Theory of FD-TDDFT in real-time and real-space

### 2.1. Time-dependent Kohn–Sham equation

The TDKS equation subject to an external laser field is given by [18,20]

$$i\hbar\frac{\partial}{\partial t}\psi_p(\mathbf{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+\frac{e^2}{4\pi\varepsilon_0}\int\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'+V_{\mathrm{xc}}+V_{\mathrm{ion}}+V_{\mathrm{ext}}\right]\psi_p(\mathbf{r},t),\tag{1}$$

where $m$ is the electron mass, $e$ is the elementary charge, and $\varepsilon_0$ is the permittivity of vacuum. This is the present working equation. $V_{\mathrm{xc}}$, $V_{\mathrm{ion}}$ and $V_{\mathrm{ext}}$ are exchange-correlation potential, electron–nuclear interaction potential, and external potential such as a laser field, respectively. The electron density $\rho$ is given by

$$\rho(\mathbf{r},t)=2\sum_{p=1}^{N/2}\left|\psi_p(\mathbf{r},t)\right|^2.\tag{2}$$

The factor of 2 indicates that each KS orbital is fully occupied (i.e., a closed shell system). To represent the XC potential, we use the following adiabatic local density approximation (ALDA)

$$V_{\mathrm{xc}}[\rho](\mathbf{r},t)\approx V_{\mathrm{xc}}^{\mathrm{LDA}}[\rho](\mathbf{r},t),\tag{3}$$

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