Journal of Molecular Structure: THEOCHEM 914 (2009) 115–129

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

Application of time-dependent density-functional theory to molecules and nanostructures

Igor Vasiliev [a], Marie Lopez del Puerto [b], Manish Jain [c,d], Alejandro Lugo-Solis [a], James R. Chelikowsky [d,e,*]

[a] Department of Physics, New Mexico State University, Las Cruces, NM 88003, USA
[b] Department of Physics, University of St. Thomas, St. Paul, MN 55105, USA
[c] Department of Physics, University of California, Berkeley, CA 94720, USA
[d] Center for Computational Materials, Institute for Computational Engineering and Sciences, University of Texas, Austin, TX 78712, USA
[e] Departments of Physics and Chemical Engineering, University of Texas, Austin, TX 78712, USA

ARTICLE INFO

Article history:
Received 25 February 2009
Accepted 17 April 2009
Available online 3 May 2009

Keywords:
TDDFT
DFT
Pseudopotentials
Optical excitations
Nanostructures
Molecules

ABSTRACT

We present *ab initio* time-dependent density-functional calculations for the optical properties of molecules, atomic clusters, functionalized carbon nanotubes, and metal-nanotube heterostructures. Our calculations are carried out in the framework of a real-space higher-order finite difference method combined with the pseudopotential approximation. In this method, the Kohn–Sham equations for electronic states are solved self-consistently on a real-space three-dimensional Cartesian grid without the use of explicit basis functions. The time-dependent density-functional linear response formalism is applied to calculate the excited-state properties of the water molecule, analyze the optical spectra of potassium atoms and clusters adsorbed on graphene and carbon nanotubes, study the assembly of organic molecules to carbon nanotubes and compute the Stokes shifts in hydrogenated silicon clusters. The results of our calculations show that the time-dependent density-functional computational approach is flexible and can be successfully applied to a variety of different physical problems.

1. Introduction

A fundamental problem in nanophysics is predicting the behavior of materials confined to small dimensions. The influence of size and geometric shape on the properties of matter become extremely important when the spatial dimensions of the system are reduced to the nanometer scale. Examples of nanoscale systems include atomic clusters, nanocrystals, quantum dots, nanotubes, nanowires, thin films, and other similar structures [1]. Nanostructures are projected to be the core elements of the next generation of technological materials that have the potential to revolutionize the design of computer chips, video screens and displays, solid-state lasers, solar cells, light detectors, and chemical sensors. It is now well recognized that the physics of nanoscale systems is dominated by the interacting electrons in an external confining potential [2]. Understanding these interactions is critical to the fabrication of nanocomposite materials with precisely controlled electronic and optical characteristics.

Theoretical studies of nanoscale systems presents major challenges to computational methods employed in quantum chemistry and condensed matter physics. The challenges are mainly related to the structural complexity and lack of three-dimensional periodicity in these systems. The complex structure and composition of nanomaterials necessitates the use of efficient numerical techniques combined with massively parallel computing. While computational methods for the ground-state properties of materials are relatively well established, calculations for the excited-state properties of nanoscale systems remain computationally demanding. When electronic excitations are explicitly included in the computational formalism, the difficulty of the calculation increases manifold. Traditionally, accurate calculations for optical excitations rely on the use of highly sophisticated techniques, such as the configuration interaction method [3], or quantum Monte Carlo simulations [4,5]. While these methods describe electronic excitations correctly, their application to complex nanostructures is constrained by high computational cost. The rapid advancement of nanotechnology has shifted the focus of materials research from the continuum solid state to nanoscale systems and emphasized the need for the development of relatively simple and accurate theoretical methods capable of predicting the optical properties of complex nanostructures from first principles. In this regard, two theoretical approaches have emerged: one is a method based on computing the frequency-dependent polarizability in the framework of time-dependent density-functional theory (TDDFT) [6–9] and the other is the Green function formalism based on solving the Bethe–Salpeter equation (BSE) [10] within the GW approximation [11]. While the GW and BSE methods have proved to be successful in predicting the band gaps and optical excitations in

---

[*] Corresponding author. Address: Departments of Physics and Chemical Engineering, University of Texas, Austin, TX 78712, USA.
E-mail address: jrc@ices.utexas.edu (J.R. Chelikowsky).

0166-1280/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2009.04.019

periodic systems, the efficiency of this formalism in application to large non-periodic systems is still being tested [12–20].

In this paper, we present a brief overview of the TDDFT formalism based on a linear response method in the frequency domain [21,22]. Within this method, a density-functional expression for the dynamic polarizability is obtained by analyzing the system response to an external periodic perturbation. The energies and oscillator strengths of electronic transitions are computed from the poles and residues of the dynamic polarizability [22]. The linear response TDDFT approach is applied to calculate the optical properties of various nanoscale systems, including inorganic and organic molecules, semiconductor nanoclusters, functionalized carbon nanotubes, and metal-nanotube heterostructures.

2. Computational methods

An *ab initio* method based on density-functional theory (DFT) [23,24] combined with the pseudopotential approximation [25] represents a quantum mechanical computational technique well suited for medium and large-scale modeling of nanomaterials. The pseudopotential method effectively reduces the total number of particles in the system by solving the quantum mechanical problem for the valence electrons only [25]. The density-functional formalism transforms the many-body Schrödinger equation into a set of single-electron Kohn–Sham equations given by[1]

$$\left(-\frac{\nabla^2}{2}+\sum_a v_{\text{ion}}(\mathbf{r}-\mathbf{R}_a)+v_{\text{H}}[\rho](\mathbf{r})+v_{\text{xc}}[\rho](\mathbf{r})\right)\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r}). \tag{1}$$

In Eq. (1), the true potential of each ion at $\mathbf{R}_a$ is replaced by a pseudopotential $v_{\text{ion}}(\mathbf{r}-\mathbf{R}_a)$ accounting for the interaction of valence electrons with core electrons and nuclei, the Hartree potential, $v_{\text{H}}[\rho](\mathbf{r})$, describes the electrostatic interactions among valence electrons, the exchange–correlation potential, $v_{\text{xc}}[\rho](\mathbf{r})$, represents the non-classical part of the Hamiltonian, and $\rho(\mathbf{r})$ is the charge density. The single-electron Kohn–Sham eigenvalues ϵ_i and eigen wave functions $\psi_i(\mathbf{r})$ in Eq. (1) pertain to valence electrons only.

The non-local ionic pseudopotential simulates the angular momentum dependent interaction between the valence and core electrons. In practical computational schemes, the Kleinman–Bylander [26] form of the non-local pseudopotential is usually employed,

$$v_{\text{ion}}(\mathbf{r}-\mathbf{R}_a)\psi_i(\mathbf{r})=v_{\text{local}}(\mathbf{r}-\mathbf{R}_a)\psi_i(\mathbf{r})+\sum_{l,m}G_{lm}\Delta v_l(\mathbf{r}-\mathbf{R}_a)\phi_{lm}(\mathbf{r}-\mathbf{R}_a), \tag{2}$$

where v_{local} is the local ionic pseudopotential, $\Delta v_l = v_l - v_{\text{local}}$ is the difference between the local potential and the potential component with the angular momentum l, ϕ_{lm} are the atomic pseudo wave functions, and the projection coefficients G_{lm} are calculated as

$$G_{lm}=\frac{\langle\phi_{lm}|\Delta v_l|\psi_i\rangle}{\langle\phi_{lm}|\Delta v_l|\phi_{lm}\rangle}. \tag{3}$$

The exchange–correlation potential is approximated by a parametrized analytical expression of the charge density. Among the common approximations for the exchange–correlation functional are the local-density approximation (LDA) [24,27] and the generalized gradient approximation (GGA) [28,29], although new types of hybrid functionals, such as B3LYP [30], are becoming increasingly popular. Owing to the non-linear nature of the exchange–correlation functional, the accuracy of the approximation can be improved by correcting the analytical formula to account for the core electronic density. The exchange–correlation potential is then evaluated as a functional of the core-corrected charge density [31],

$$\rho(\mathbf{r})=\rho_v(\mathbf{r})+\sum_a\rho_{\text{core}}(|\mathbf{r}-\mathbf{R}_a|), \tag{4}$$

where $\rho_{\text{core}}(|\mathbf{r}-\mathbf{R}_a|)$ is a fixed partial correction for the charge density of core electrons and $\rho_v(\mathbf{r})$ is the charge density of valence electrons calculated as

$$\rho_v(\mathbf{r})=\sum_i n_i|\psi_i(\mathbf{r})|^2, \tag{5}$$

where $\psi_i(\mathbf{r})$ are single-electron wave functions and n_i are occupation numbers.

The combination of the Kohn–Sham scheme, exchange–correlation approximation, and pseudopotential method reduces the overall computational cost without significant loss of accuracy. Furthermore, calculations performed in the framework of the DFT method do not require any adjustable external parameters [32]. The absence of structure and material-dependent parameters and a relatively low computational cost makes the *ab initio* DFT approach applicable to complex nanosystems containing hundreds or, in some cases, thousands of atoms [33,34].

The central theorem of DFT states that the external potential and the ground-state energy of a system of interacting electrons are uniquely determined by the ground-state charge density [23]. However, the original formulation of the DFT formalism has been restricted to the *time-independent* case only. A proper treatment of electronic excitations is not possible within the time-independent framework. This limitation has led to the development of *time-dependent* density-functional theory (TDDFT), which extends the central DFT theorem to time-dependent phenomena [6–9]. The TDDFT formalism can be used to calculate absorption spectra and predict optical properties of nanostructured materials. Similarly to time-independent DFT developed by Kohn and Sham, TDDFT reduces the many-electron problem to a set of self-consistent single-electron equations,

$$\left(-\frac{\nabla^2}{2}+v_{\text{eff}}[\rho](\mathbf{r},t)\right)\psi_i(\mathbf{r},t)=i\frac{\partial}{\partial t}\psi_i(\mathbf{r},t). \tag{6}$$

However, the single particle wave functions, $\psi_i(\mathbf{r},t)$, and the effective potential, $v_{\text{eff}}[\rho](\mathbf{r},t)$ in Eq. (6) explicitly depend on time. The effective potential is given by

$$v_{\text{eff}}[\rho](\mathbf{r},t)=\sum_a v_{\text{ion}}(\mathbf{r}-\mathbf{R}_a)+\int\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+v_{\text{xc}}[\rho](\mathbf{r},t). \tag{7}$$

The three terms on the right side of Eq. (7) describe the external ionic potential, Hartree potential, and the exchange–correlation potential, respectively. The time-dependent charge density is defined as $\rho(\mathbf{r},t)=\sum_i n_i|\psi_i(\mathbf{r},t)|^2$, where n_i are occupation numbers.

Electronic excitations can be calculated in the framework of TDDFT by considering a linear response to an external periodic perturbation [21,22]. In this approach, the linear response formalism is used to derive a density-functional expression for the dynamic polarizability. The excitation energies Ω_I, which correspond to the poles of the dynamic polarizability, are obtained from the solution of an eigenvalue problem

$$\mathbf{Q}\,\mathbf{F}_I=\Omega_I^2\mathbf{F}_I, \tag{8}$$

where the matrix $\mathbf{Q}$ is given by

$$Q_{ij\sigma,kl\tau}=\delta_{i,k}\delta_{j,l}\delta_{\sigma,\tau}\omega_{kl\tau}^2+2\sqrt{\lambda_{ij\sigma}\omega_{ij\sigma}}K_{ij\sigma,kl\tau}\sqrt{\lambda_{kl\tau}\omega_{kl\tau}}. \tag{9}$$

In this equation, the indices i,j, and σ $(k,l$, and $\tau)$ refer to the space and spin components, respectively, of the unperturbed static

---

[1] Atomic units $(\hbar=e=m=1)$ are used throughout this chapter.