

Localized-Density-Matrix Method, and its Application to Carbon Nanotubes

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ABSTRACT

The localized-density-matrix (LDM) method [Yokojima and Chen, Chem. Phys. Lett. **292**, 379 (1998)] is employed to simulate the optical responses of very large carbon nanotubes. The PPP and PM3 Hamiltonians are used to describe the electrons in the systems, and the time-dependent Hartree-Fock (TDHF) approximation is employed to calculate the linear optical responses. Real space reduced density matrices for different oscillators are examined, and thus the nature of dipole activated excitations is understood.

I.

INTRODUCTION

Carbon nanotubes (Iijima, 1991), which are graphite sheets rolled up in a cylindrical form, are expected to present very interesting optical properties. Carbon nanotubes are quite large, thus are computationally difficult to characterize their excited states properties. Recently the linear scaling LDM method has been developed to evaluate the properties of both ground and excited states (Yokojima and Chen, 1998; Liang *et.al.* 1999; Yokojima and Chen, 1999; Yokojima and Chen, 1999). It is based on the TDHF approximation (Ring and Schuck, 1980) and the truncation of the ground and excited state reduced single-electron density matrices. Its computational time scales linearly with the system size N . The method has been tested successfully to evaluate the optical and ground state properties of conjugated polymers with die orthogonal and non-orthogonal basis sets (Yokojima and Chen, 1998; Liang *et.al.* 1999; Yokojima and Chen, 1999; Yokojima and Chen, 1999). In this work we apply the LDM method to calculate the absorption spectra of a series of carbon nanotubes. In order to understand the nature of various electronic excitations, we examine the reduced density matrices corresponding to these excitations.

II. MODEL

The effective Hamiltonian can be written as

$$H = H_e + H_{ee} + H_{ext}. \quad (1)$$

Here H_e is one-electron part of the Hamiltonian, which is similar to the tight binding model. H_{ee} describes the effective Coulomb repulsion among electrons. H_{ext} represents the effects of the external field. The PPP Hamiltonian considers only the π electron while the PM3 model includes all valence electrons (2s, 2p_x, 2p_y, and 2p_z). H_{ee} is of different form for the PPP and PM3. Details can be found in references (Takahashi and Mukamel, 1994; Stewart, 1989).

III. TDHF AND LDM METHODS

Within the TDHF approximation, the reduced single-electron density matrix satisfies the following equation of motion

$$i\hbar \frac{d}{dt} \rho(t) = [h(t) + f(t), \rho(t)], \quad (2)$$

where $h(t)$ is the Fock matrix, $f(t)$ describes the interaction between an electron and the external field $E(t)$ (Takahashi and Mukamel, 1994). For the linear response of optical properties, its dynamics may be described by the following equation,

$$\begin{aligned} i\hbar \left(\frac{d}{dt} + \gamma \right) \delta \rho_{ij}^{(1)} = & \sum_k (h_{ik}^{(0)} \delta \rho_{kj}^{(1)} - \delta \rho_{ik}^{(1)} h_{kj}^{(0)}) \\ & + \sum_k (\delta h_{ik}^{(1)} \rho_{kj}^{(0)} - \rho_{ik}^{(0)} \delta h_{kj}^{(1)}) + \sum_k (f_{ik} \rho_{kj}^{(0)} - \rho_{ik}^{(0)} f_{kj}). \end{aligned} \quad (3)$$

Here, a phenomenological parameter γ is introduced to simulate the dephasing process.

The computational time for solving Eq. (3) scales as $O(N^{3-4})$ and thus the conventional TDHF is limited to systems of moderate size. However, carbon nanotubes may contain more than thousands of atoms. The LDM method is of $O(N)$ scaling, has been applied to systems with ten thousand atoms, and is thus suitable to calculate the excited state properties of carbon nanotubes. The following approximations

$$\begin{aligned} \text{(a)} \quad \rho_{ij}^{(0)} = 0 & \quad \text{if } r_{ij} > l_0, \\ \text{(b)} \quad \delta \rho_{ij}^{(1)} = 0 & \quad \text{if } r_{ij} > l_1 \end{aligned}$$

are the immediate consequence of the nearsightedness of reduced density matrix, and lead directly to

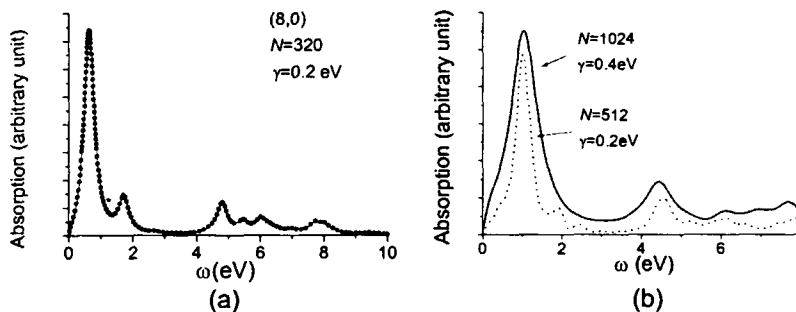


Figure 1: (a) Comparison between TDHF (circle) and LDM (solid line) for $N=320$. (b) $N=512$ (dashed line) and $N=1024$ (solid line).

$$(c) \quad h_{ij}^{(0)} = 0 \quad \text{if } r_{ij} > l_0,$$

$$(d) \quad \delta h_{ij}^{(1)} = 0 \quad \text{if } r_{ij} > l_1.$$

With (a), (b), (c), and (d), the range of the summation $\sum_{ij} \delta \rho_{ij}^{(1)}$ is limited to a finite region for each term of the r.h.s. of Eq. (3). $\delta \rho_{ij}^{(1)}$, the computational cost for each $\delta \rho_{ij}^{(1)}$ is finite (i.e. not depending on N). Since only $O(N)$ number of $\delta \rho_{ij}^{(1)}$ are to be determined [because of (b)], the total number of computational steps are then $O(N)$ as well.

IV. RESULTS

Figure 1 shows the comparison calculated by full TDHF (circle) and LDM (solid line) for $C_N H_{16}$ ($N=320$) with chiral vector (8,0). Cut-off lengths are chosen to cover 15 rings for both l_0 and l_1 . From the figure, we can clearly see the result with the linear-scaling LDM method agrees to the full TDHF result very well. Thus we employ these cut-off lengths to calculate $N=512$ (32 rings) and $N=1024$ (64 rings). The results show the oscillator strength of the first peak becomes less and tends to zero as N increases. We also investigate the tubes (9,0) $C_{576} H_{18}$ and (10,0) $C_{640} H_{20}$. Figure 2 shows absorption spectra for C_{108} , C_{60} , and $C_{48} H_{16}$ based on the PM3 model. There is a marked difference between three spectra. The difference between the first peak position of $C_{48} H_{16}$ and C_{108} indicate that the caps are playing an important roll for the smaller size carbon nanotube. The character of those peaks may be revealed by examining their density matrices.

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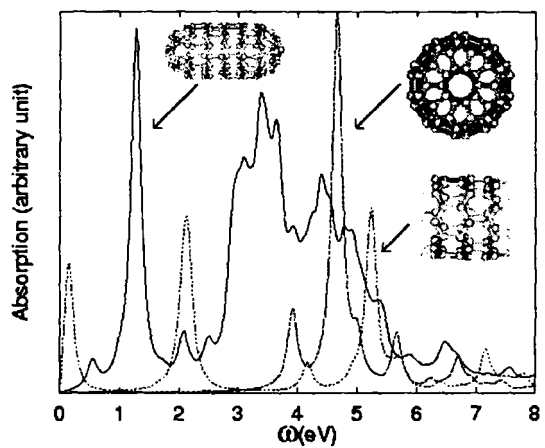


Figure 2: Absorption spectra with PM3 model. C_{108} (solid line), C_{60} (long dashed line), and $C_{48}H_{16}$ (short dashed line).