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# Numerical Study of Materials for Optical Properties – Predictions for Materials Design –

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Time dependent density functional theory has been applied to the study of optical responses in conjugated polymers such as poly (9,9-dialkyl-fluorene) and dielectric responses in semiconductors such as C, Ge, Si, and AlGaAs. In this study, real-space and real-time calculation techniques are used for the electronic states instead of the conventional basis-expansion techniques. Our method seems more efficient since a relatively small number of meshes is required for obtaining results with reasonable accuracy, which depends on an adjustable parameter, the total number of time steps. The methods and the calculations for optical and dielectric properties will be described in detail.

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## Introduction

Recent fast technical innovations in IT-related materials together with the Internet accelerate the development in communication technologies, and flat panel display devices for PCs, cellular telephones and TVs. We have to note that many optical materials have been newly developed as well. At the same time, evolution of computer technology and its application also drive material development, which takes advantage of the technique to calculate and predict the material properties. Nowadays, large-scale calculations, which were impossible until a few years ago, are regularly carried out, and the results are effectively utilized and fed back to material development.

In traditional quantum chemistry, only HOMO and LUMO are calculated as indicators for the wavelength in absorption and emission as optical properties in light emitting materials. However, it is not enough for some purposes as only limited information such as the energy band gap has been considered. On the other hand, one of the computational progress in the last few years has been seen in many applications of Density Functional Theory (DFT)<sup>1)–4)</sup>. This theory provides us a big progress in the computations; fairly large scale of molecules can be easily handled while keeping a good accuracy. The theory has also been introduced into typ-

ical quantum chemistry programs recently.

Many improvements, such as the Car-Parrinello type method<sup>7)</sup> and the conjugate gradient method<sup>8), 9)</sup>, have been introduced to DFT to enhance the computational efficiency. At the same time, Time Dependent Density Functional Theory (TDDFT) has been focused recently as an advanced technique.<sup>10), 11)</sup> Since DFT is a theory based on the ground state, it also involves difficulties to describe the excited state, which is important for luminescence. TDDFT is expected to provide some information about this issue. We have also been applying this technique to the research of light emitting materials as in polymer light emitting diodes (PLEDs). In this report, we will introduce TDDFT and its application together with some examples of our results, and developments for the future.

The outline of this report is as follows. After the simple explanation of TDDFT, we will introduce some of our results in the analysis of emission and absorption spectra, dielectric constants and optical properties. Then a summary and discussion for future development will be presented.

## Time Dependent Density Functional Theory

In the analysis of materials, we have to calculate the electronic state, where the important but difficult point

is that one has to solve many body problems. Since it is difficult to solve the equations for many interacting electrons, we usually adopt a one-electron approximation. In order to describe exchange correlation interaction based on many body problems, the exchange correlation term is introduced in DFT. The history of DFT is long and it is based on the work of Hohenberg and Kohn in 1964 that total energy of an externally interacting system is described as a functional of the charge density, and the proof of Kohn and Sham in 1965 that the total energy of the ground state can be derived from the one particle wave functions of an independent system.<sup>1), 2)</sup> The fundamental equation for DFT is called the Kohn-Sham equation in (Eq. 1).

$$\left\{ -\frac{1}{2} \nabla^2 + \sum_a V_{ion}(\vec{r} - \vec{R}_a) + V_{e-e} + \mu_{xc}(n(\vec{r})) \right\} \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \quad (\text{Eq. 1})$$

where  $V_{ion}(\vec{r} - \vec{R}_a)$ ,  $V_{e-e}$  and  $\mu_{xc}$  represent the atom-electron interaction, the coulomb interaction between electrons, and the exchange correlation potential, respectively. In this report, the atomic unit  $\hbar/2\pi = m = e^2 = 1$  is adopted for all cases except the explicit notation. Electronic charge density is given by  $n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$  and  $\psi_i(\vec{r})$  denotes the wave function of electrons where  $i$  is the index of the band. DFT has been widely used because the exchange correlation term is expressed in the general form described by the exchange correlation energy functional in the locally uniform electron density. Many improvements have been still developed and proposed.

Since DFT is a theory based on the ground state, it is insufficient to describe the excited states. To solve this limitation, in 1984, Runge and Gross have proposed Time Dependent Density Functional Theory (TDDFT), in which some of information about the excited state is contained in the time dependent electronic state.<sup>10)</sup>

$$\left\{ -\frac{1}{2} \nabla^2 + \sum_a V_{ion}(\vec{r} - \vec{R}_a) + V_{e-e} + \mu_{xc}(n(\vec{r}, t)) + V_{ext}(\vec{r}, t) \right\} \psi_i(\vec{r}, t) = i \frac{\partial}{\partial t} \psi_i(\vec{r}, t) \quad (\text{Eq. 2})$$

This method is effectively used for the cases where the potential is dependent on time, such as the time-dependent behaviors of electrons in oscillating electric and magnetic fields, and chemical reactions in which the adiabatic approximation does not work. In these phenomena, we have to take into account the excited

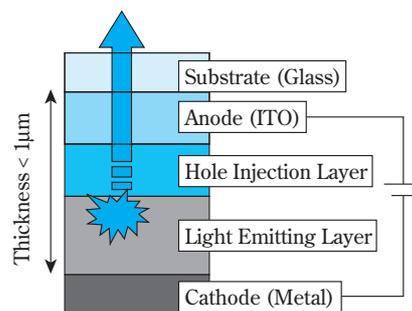
states. Empirically, we know that these are described fairly well by TDDFT. However, since this method is, of course, also based on DFT, the results are theoretically guaranteed only for the ground state. Or, this method has been developing in a sense.

The conventional method in electronic structure calculations is a basis-expansion technique where plane waves, atomic orbitals, or gaussians are used to describe the wave functions as basis functions. On the other hand, in our calculation, real-space and real-time approaches are employed without any basis functions.<sup>11)</sup> One of the advantages is that we can keep our program simple and understand physical meanings as directly as possible. The time revolution is performed in real time, thus the total number of time steps is closely connected to the accuracy. To realize it, enough computational resources are required. However, it could be matched by recent progress in computers.<sup>12)</sup>

In Gaussian, well-known as conventional quantum chemical commercial software, TDDFT has also been introduced and utilized as a simplified method through Random Phase Approximation (RPA), which is one of the fundamental approximations in many body problems.<sup>13)</sup> In practical work for our material research, we also use it together with our real-space and real-time method.

## Analysis of Light Emission and Absorption Spectra

Polymer light emitting diodes (PLEDs) have been of interest for displays and other lighting applications. As shown in Fig. 1, one of the main features of PLEDs is their having a simple structure where a light emitting layer is sandwiched between electrodes, anode and cathode. The radiative recombination of the injected electrons and holes in the light emitting layer result in



**Fig. 1** Structure of Polymer LED

the emission of light. Since the emission color is determined by the nature of the polymer in the emitting layer, the prediction of optical properties of the light emitting material is extremely important in PLED development.<sup>14)</sup>

In this section, we will focus on the absorption and emission spectra of the polymers. For this purpose, we have been applying TDDFT, which has been widely used and recognized as a powerful and one of the most suitable tools in studies of the optical properties of materials.<sup>15)</sup>

The calculation procedure is as follows. First, we have to compute the optimized electron density for a given structure in its ground states by means of time independent density functional theory (DFT) with Local Density Approximation (LDA).<sup>3), 4)</sup> In our method, the real-space uniform mesh representation is used for the electron wave functions in contrast to a conventional expansion technique by basis sets on each atom. Thus, the mesh size is directly related to the accuracy in the calculations and a mesh size of  $d \sim 0.3 \text{ \AA}$  was used in all calculations in this section. With this mesh size, a precision in the order of 0.1 eV can be achieved in the energy of systems with hydrocarbons.

Then, we applied an external field to the system as a perturbation

$$\psi_i(t=0) = e^{ikx} \psi_i(0) \quad (\text{Eq. 3})$$

(here,  $e^{ikx}$  expresses a perturbation in the  $x$  direction at  $t=0$ , corresponding to an instantaneously applied electric field in the  $x$  direction) and followed the linear responses of the system in real time. The time evolution of the wave function is expressed by the time evolution operator in (Eq. 4), and the Taylor expansion of the time evolution operator up to the 4<sup>th</sup> order was used in our calculations.

$$\psi_i(t) = e^{-iHt} \psi_i(0) \quad (\text{Eq. 4})$$

The optical response can be found from the strength function  $S(\omega)$  in the following equation,

$$S(\omega) = \frac{2m\omega}{\pi\hbar e^2} \text{Im} \alpha(\omega) \quad (\text{Eq. 5})$$

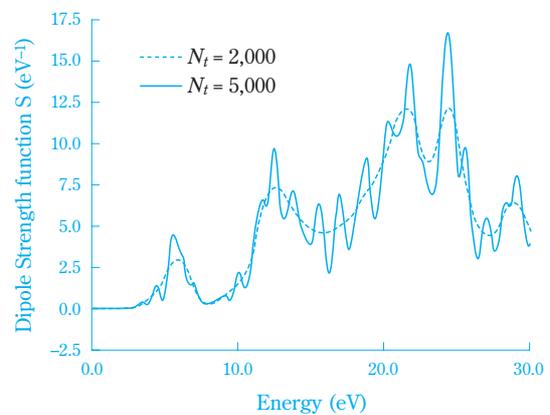
where  $\alpha(\omega)$  is the dynamic polarizability given by (Eq. 6).

$$\alpha(\omega) = \frac{1}{k} \int dt e^{-i\omega t} \mu(t) \quad (\text{Eq. 6})$$

Here  $\mu(t)$  is the time dependent dipole moment given by (Eq. 7).

$$\mu(t) = \frac{e^2}{\hbar} \int dt e^{i\omega t} xn(\vec{r}, t) \quad (\text{Eq. 7})$$

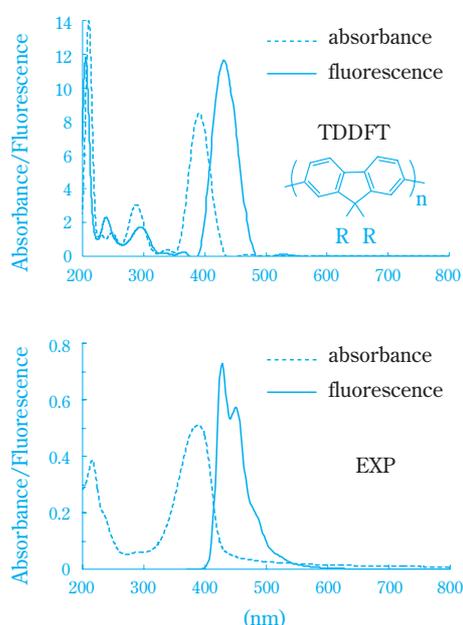
In the real-time calculations, the width of the time steps  $\Delta t$  and the total number of time steps  $N_t$  have to be considered as important parameters. As an example, the effect of the total time steps  $N_t$  on spectra is shown in Fig. 2 where the molecule C<sub>60</sub> is considered. The solid and dashed lines correspond to the case of  $N_t=5000$  and 2000 respectively, and time step  $\Delta t=0.001 \hbar/eV$  is used for both cases. The energy resolution is clearly improved in the former,  $N_t=5000$ . In particular, one can clearly see low energy absorption peaks at  $\sim 3.5$ ,  $\sim 4.4$  and  $\sim 5.6$  eV, which agree well with the experimentally observed peaks at  $\sim 3.8$ , 4.8 and 5.8 eV. Since these peaks cannot be seen for  $N_t=2000$ , the time evolution is considered as insufficient. As can be seen from this example, the total number of time steps is an important parameter and determines the effective energy resolution in calculated spectra. In addition, the time step  $\Delta t$  is short enough so that the Hamiltonian can be conserved. These are important points for TDDFT in real time technique. As our preliminary test,  $T=10\hbar/eV$  gives the energy resolution of  $\hbar/T=0.1eV$  for hydrocarbons. In our calculations, the Troullier-Martins pseudopotentials<sup>5), 6)</sup> in the separable form and the local density approximation (LDA) for exchange-correlation potential<sup>3), 4)</sup> are used. One of the advantages of the real-space and real-time approach is that the CPU time scales with the number of particles  $N$  and the spatial dimension  $D$  as  $N_a D \sim N^2$ , which becomes advantageous especially when we need to handle a



**Fig. 2** Strength function of the molecule C<sub>60</sub>. The solid and dashed lines correspond to  $N_t=5,000$  and 2,000, respectively

large system. Another advantage of the real-space and real-time calculation is that one can obtain spectra in the whole energy region by a single calculation as in Fig. 2.

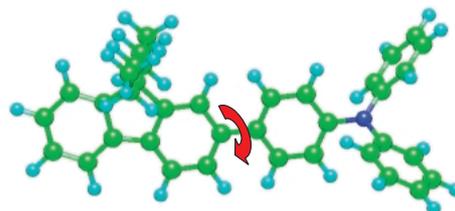
Fig. 3 shows the results of the absorption and emission spectra for 9,9-dialkyl-fluorene, which is well known as a blue emitting material in PLED. One can find extremely good agreement between computed and experimental spectra in both their spectrum shape and also their peak wavelength. In particular, the absorption peak wavelength at  $\sim 390\text{nm}$  is reproduced extremely well. For fluorescent spectra, one can also see a good agreement in the main peak at  $\sim 420\text{nm}$  between calculation and experiment, even though there exists a sub-peak at  $\sim 450\text{nm}$  only in experiment.<sup>16)</sup>



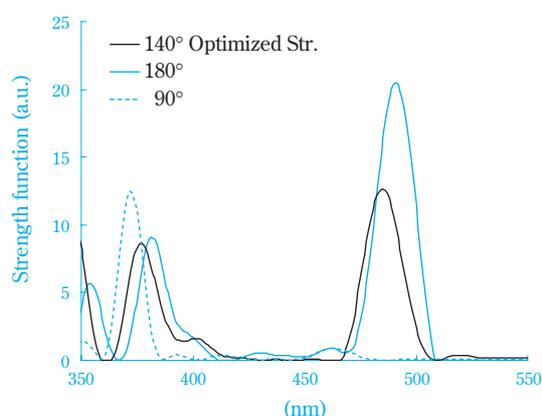
**Fig. 3** Calculated (upper) and experimental (lower) optical properties of fluorene

We have also carried out an analysis of a fluorene-amine system in order to study the effect of dihedral angle on absorption spectrum. The structures of 9,9-dipropylfluorene and triphenylamine are shown in Fig. 4. The dihedral angle between two units is changed systematically and the spectrum is computed for each configuration. The structure with the dihedral angle of  $\sim \pm 140^\circ$ , which is the most stable in energy, has the absorption spectrum at  $\sim 485\text{nm}$ . When it is  $\pm 180^\circ$ , where the benzene rings are parallel, the peak wavelength is red-shifted to  $\sim 490\text{nm}$ , and the absorption strength is increased. On the other hand, in the neighborhood of  $\pm 90^\circ$  where the benzene rings are perpendicular to each other, the peak wavelength is blue-shift-

ed to  $\sim 370\text{nm}$  without a big change in absorption strength. These observations are related to the degree of wave function localization, that is, the more the wave function is delocalized, the longer peak wavelength is obtained.



**Fig. 4** Dihedral angle between 9,9-dipropyl-fluorene and triphenylamine, whose angle is  $\pm$  about  $140^\circ$  in the optimized structure



**Fig. 5** Dihedral angle dependence of absorption spectra

As we have discussed so far, TDDFT is a powerful tool to study the optical properties of materials, thus it can be applied to designing molecular structures with desired optical properties.

### Calculations of Dielectric Constants and Optical Constants

Dielectric functions, as an important property of electronic devices, depend on the material structures, which variously change in the process to find dynamic properties. The dielectric function is usually obtained as a response of a static electronic eigenstate to external perturbation. From this point of view, TDDFT is expected as a new and capable technique to calculate time dependent phenomena such as optical properties or dielectric functions. For example, transconductance, which is a measure of current carrying capability of

electronic devices, is directly related to the dielectric function of a material. Thus, the large possibility is that the calculation of this property can provide us with a prediction of characteristic features of a device.<sup>17), 18)</sup>

Calculation procedures are as follows. Some modification of the basic TDDFT equation in (Eq. 2) is necessary as our major target materials are solids such as semiconductors and oxides. Hamiltonian of the system is written with the coulomb field  $V(\vec{r})$  and the vector gauge field  $\hat{z}A(t)$  which express the interactions between electrons and electromagnetic fields, and satisfies the periodic boundary condition. This gauge field is constant and independent on  $\vec{r}$ . The electric field can be written in (Eq. 8).

$$\vec{E} = -\vec{\nabla}V - \hat{z} \frac{dA}{dt} \quad (\text{Eq. 8})$$

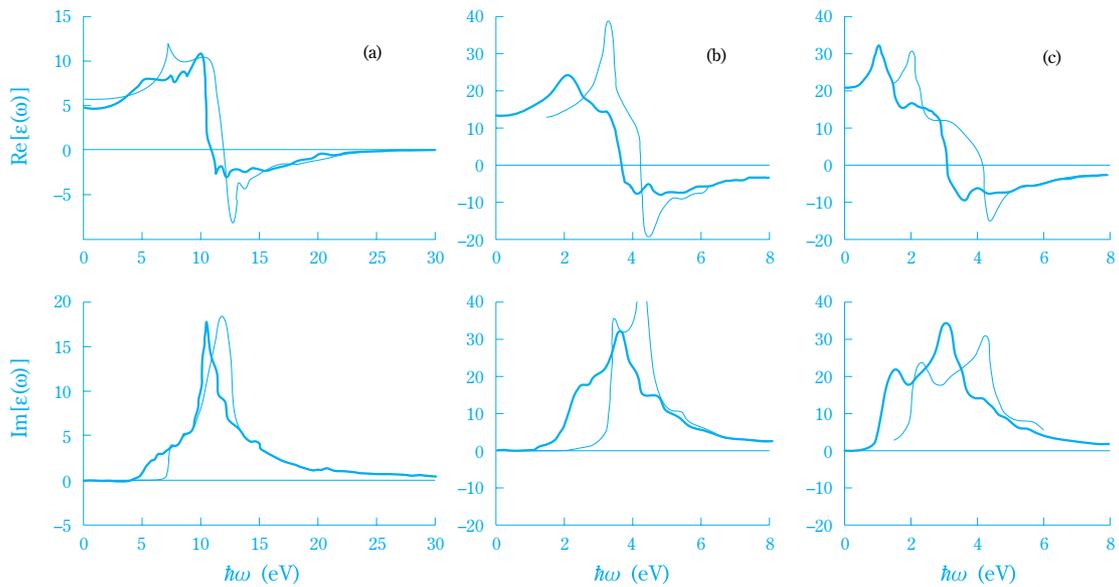
With these fields, we can write Lagrangian of the system and derive the generalized equations of motion, which provides the dielectric function (see the details in reference 8). In our calculations of the dielectric function, the perturbation  $A(0^+) = A_0$  is applied at  $t=0$ , which corresponds to an instantaneously applied electric field at  $t=0$ . As the polarization is given by  $-dA(t)/dt$ , the time evolution is carried out for a surface charge  $\sigma(t) = dA(t)/4\pi dt$ . The dielectric function  $\epsilon(\omega)$  in (Eq. 9) is calculated as a Fourier component for the polarization field.

$$\frac{1}{\epsilon(\omega)} - 1 = \frac{1}{A_0} \int_{0^+}^{\infty} e^{i\omega t - \eta t} \frac{dA(t)}{dt} dt \quad (\text{Eq. 9})$$

where  $\eta$  is a small quantity to introduce the imaginary part of  $\epsilon(\omega)$ .

In our calculation, first the static electronic ground state, under the condition  $A=0$ , is calculated in a real space with a uniform mesh. Then, the time evolution is carried out from this optimized electronic state. As in the case of molecule calculations, the mesh spacing is related to the accuracy in energy. For example, from our preliminary study of periodic systems, mesh spacing of  $\Delta x \approx 0.3 \text{ \AA}$  is required for the carbon systems to have an accuracy of 0.1 eV in energy. In this study, we have used mesh spacing of  $\Delta x \approx 0.3 \text{ \AA}$  for carbon and  $\Delta x \approx 0.45 \text{ \AA}$  for other atoms. In TDDFT calculations, the time step  $\Delta t \approx 0.001 \hbar/eV$  is used. The total number of time steps  $N_t$  affects the resolution of response, especially in the low energy region, and the time evolution is done up to  $N_t = 20,000$  for all cases. This seems enough to reproduce the dielectric function with fairly good accuracy. We use a cubic unit cell with 8 atoms for all periodic systems in this report. Each cell is divided into  $16^3$  points for carbon systems and  $12^3$  points for other systems to represent the Bloch states. Throughout the calculations, we use the Troullier-Martins pseudopotential with a separable form<sup>5), 6)</sup> for the external potential and the local density approximation (LDA)<sup>3), 4)</sup> for the exchange-correlation energy.

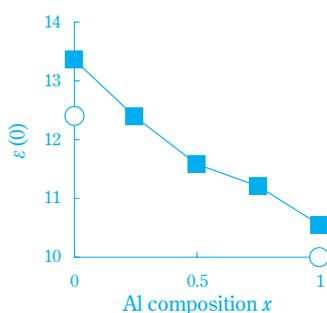
The dielectric properties of elemental semiconductors (C, Ge, Si) are shown in Fig. 6, 7 and 8. In our calculations, spurious plasmons have been observed



**Fig. 6** The real and imaginary part of the dielectric functions for (a) diamond, (b) silicon and (c) germanium. Thick and thin lines represent the calculated and experimental value, respectively

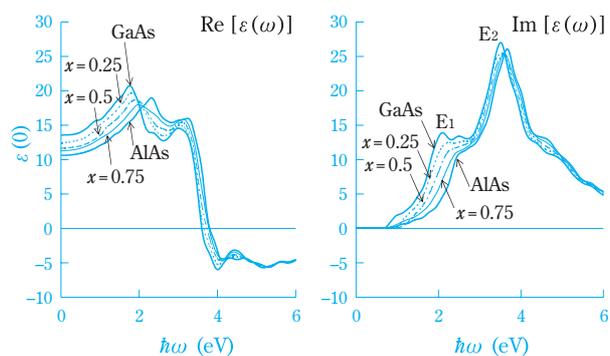
inside the band gap. Since they are artifacts, we have excluded them by considering the imaginary part of the responses  $\text{Im } \varepsilon(\omega)$  from the value of the calculated band gap. Then, the real part  $\text{Re } \varepsilon(\omega)$  is determined through the Kramers-Kronig relation. As our calculation is carried out within the frame work of LDA, the band gap tends to underestimate. However, in all cases, the dispersion of the dielectric function is reproduced fairly well both in the real and the imaginary part. Even though some differences in the higher energy region have been observed, the calculated values in the lower energy region are in good agreement with experiments.<sup>19)</sup> Especially, good agreement in the whole energy region has been obtained in the carbon system and, especially, the static dielectric function  $\varepsilon(0)$  agrees extremely well with experiments.

For a compound semiconductor  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , the static dielectric constant  $\varepsilon(0)$  is plotted as a function of the components of aluminum in Fig. 7. It monotonously decreases with the components from 13.36 for  $x=0$  to 10.60 for  $x=1$ , which is in good agreement with the experimental values of 12.4 for  $x=0$  and 10.06 for  $x=1$ .<sup>20)</sup> Near the point  $x=0.45$ , it has been known that the energy band separation between the conduction band minimum and the top of the valence band changes from  $\Gamma$  to X. Our static dielectric function  $\varepsilon(0)$  also shows the effect of this change.



**Fig. 7** The calculated static dielectric constant shown by squares is plotted as the composition of aluminum  $x$  in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$

Fig.8 shows the frequency dependence of the dielectric function for the compositional ratio  $x$  of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . In the imaginary part of the dielectric functions, which correspond to the absorption spectra, there are two peaks: the first peak  $E_1$  ( $\sim 2.0\text{eV}$ ) and the second peak  $E_2$  ( $\sim 3.5\text{eV}$ ) can be identified with the parallel bands along  $\Lambda$  and  $\Delta$ , respectively. Both values are underestimated in energy. This underestimation is well known



**Fig. 8** Dielectric properties of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . Solid lines represent those of GaAs and AlAs respectively. Dashed, dashed-dotted and dashed-two-dotted lines show those of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x=0.25, 0.5, 0.75$ ). Calculated static dielectric constants  $\varepsilon(0)$  are 13.36( $x=0$ ) and 10.60( $x=1$ ), compared to those of experimental values 12.4( $x=0$ ) and 10.06( $x=1$ )

in LDA and is an important issue to be improved in the near future.

The dielectric function in this report is due to electronic polarization, not to orientational polarization, which is not taken into account in this calculation. In addition, the refractive index  $n$  and the extinction coefficient  $k$  are quite important quantities in optical materials and those can be derived from this dielectric function.

In this section, we have applied TDDFT technique to calculate the dielectric functions and optical properties in solids formed from simple species and compositions. Theoretically, it is also applicable to various larger systems including layered structures as in real electronic devices. We believe that this type of calculation will be carried out in much faster computers developed in the near future.

## Summary and Future Developments

As a recent topic, a real space and real time calculation technique for TDDFT has been introduced. This theory provides some parts of the information about excited states, and is expected as a new technique to study the optical properties of light emitting materials. In this report, we have discussed some of our results about optical properties of conjugated polymers and the dielectric functions of semiconductor materials.

As the features of this method, we can obtain fairly good agreement with experimental results through

calculation with a relatively small number of meshes, and the total number of time steps in the time evolution is related to the accuracy of physical properties such as optical spectra and dielectric functions. From this point of view, these properties can be conveniently calculated in a required energy region with desired accuracy. To realize this, of course, sufficient computing resources are required.

We are now confident that the important time dependent electric and optical properties for the development of materials are provided by TDDFT, which is expected to be one of our future foundational techniques.

In this report, we have been limited to a brief introduction of TDDFT. Further and more detailed explanations of this technique can be found in the references cited.

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