§33. Numerical Study of Plasma and Condensed Matter in Electromagnetic Fields

Zempo, Y. (Hohsei Univ.), Tanaka, M. (Chubu Univ.)

The time-dependent density functional theory (TDDFT) has become one of the most prominent method and is most widely used for the calculation of excited states of medium-sized to large molecules. It is recognized as a powerful tool for optoelectronic behaviors. TDDFT is in principle capable of treating these sorts of behaviors, if the exact local exchange-correlation functional is known. Our TDDFT is performed in real-time real-space by stimulation of the external electric field, and the dynamic dipole moment is calculated for the optical properties. The advantage is that it is possible to describe and recognize the electronic dynamic motion such as plasma motions directly, and quite easy to parallelize.

In the Annual Report of 2015, we have applied our TDDFT to 11-cis retinal to investigate the optical absorption in optical wavelength. This material is capsulated in an opsin molecule [1]. Because of the polyene structure in the molecule, the long-range asymptotic interaction plays an important role in the exchange energy [2, 3].

As the exchange-correlation functional, we use the usual LDA and B88, which is the simplest GGA to describe the correct asymptotic behavior.

$$\lim_{r \to \infty} \rho^{-1} \bar{E}_x = -\frac{1}{2r} \tag{1}$$

It is quite conventional to check this effect to the accuracy of the calculations. Most of GGA's such as PBE and PW91 are not satisfied with this condition. The calculated result of B88 is closer to that of experiment, compared to that of LDA. Although we have also examined other GGA's above, the results is that the spectra are close to that of LDA. Our results indicate that, if the functional to express the correct asymptotic form is selected, more accurate results can be obtained.



Fig1. Comparison of spectra: Solid line shows the result of TDDFT (LDA); Dashed line shows that of TDDFT (B88); Dotted line shows that of experiment. The spectra are normalized by the peak around 1.0-3.0eV.

In our TDDFT calculation, the peak position is confirmed by the maximum entropy method (MEM), which is applied to the spectrum analysis to find the peak related to the optical absorption effectively. Our MEM treats the repeated time-series data with an appropriate phase, which provides the efficient peak search in the spectrum analysis without any peak shift caused by the artificially repeated time series data. The technique is thoroughly explained in Ref [4].

In Fig.1, we compare the spectra calculated by TDDFT (LDA) and TDDFT (B88) with that of the experiment [5].



Fig2. The result of our MEM compared with that of FT. In our MEM, we have repeated 100 times repeated time-series of 12,000 data with phase correction $(-3/4\pi)$ and the Low Pass Filter, whose cut off is 3.0eV. The maximum lag is M= 3,000.

The calculated spectrum generally tends to become broad and weak in the lower energy region, if we have enough time-evolution. However, it is restricted by the calculation time, which is finite. Also, what we are interested in is that the lower energy related to the energy gap and optical observations. Thus, for the effective spectrum analysis, we apply our newly developed MEM with low-pass filter. In Fig.2, there is a peak around 2.8eV, which is due to the lowpass filter to reduce the higher energy spectrum.

From this calculation, we can obtain the first peak at 1.30eV for LDA and 2.08eV for B88, respectively. The corresponding experimental peak is observed at around 2.9eV. The result of B88 is much closer to it. This indicates that, if we use TDDFT together with an appropriate exchange-correlation functional to express the asymptotic behavior in the long-range region, it is possible to calculate the spectrum so as to reproduce that of the experiment.

Our technique is not restricted in the optical properties but other excited states, whose interactions are relevant to plasma and materials. We will examine our technique in various fields in future.

- [1] Protein Data Bank Japan, http://pdbj.org/mom/147
- [2] K. Yabana, and G. F. Bertsch, Int. J. Quant. Chem, 75, 55 (1999)
- [3] Y. Zempo, N. Akino, M. Ishida, M. Ishitobi, and Y. Kurita, J. Phys.: Cond. Matt., 20, 064231 (2008).
- [4] M. Toogoshi, S. S. Kano, Y. Zempo, J. Comput. Chem. Jpn., 14, 71 (2015).
- [5] S. Tanaka, M. Toogoshi, Y. Zempo, J. Comput. Chem. Jpn., 14, 203 (1969)