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Maximum Entropy Method Applied to Time-series Data in Real-time Time-Dependent Density Functional Theory

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We proposed that, as an effective MEM analysis, we use the concatenated data set made from the several-times repeated raw data with an appropriate phase shift. We have applied this technique to the spectral analysis of the time dependent density functional theory (TDDFT), which is an expensive First-Principles calculations, and mainly calculate the dynamic dipole moment as an electron dynamics. The results are quite efficient, because even short time evolution provides clear peak position as the lower frequency region. Also, the higher resolution can be obtained, which is closer to that of FT with practically time-evaluated data as the same total number of time steps.

I. Introduction

First-Principles calculation especially Time dependent density functional theory (TDDFT) will be one of the key techniques for materials development of optical properties, because a certain level of information of excited states can be described.

- **We use simple electron dynamics style TDDFT to obtain the excited states. Just we use is the ground states and a que potential.**
- **For real-time evolution, we need lots of time steps relevant to the spectrum resolution. Long time steps decides the resolution of the results from Fourier transformation (FT) .**
- **Our challenge is to replace this FT with MEM**

II. Real-time Time dependent density functional theory (TDDFT)

1. TDDFT (real-time)

$$i\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = H_{KS}[\rho]\psi(\boldsymbol{r},t)$$

Runge-Gross, PRL52(1984) [1]

$$\psi(\boldsymbol{r},t+\Delta t) = \exp[-iH_{KS}[\rho(t)]\Delta t]\,\psi(\boldsymbol{r},t)$$

Yabana-Bertsch, PRB54 (1996) [2]

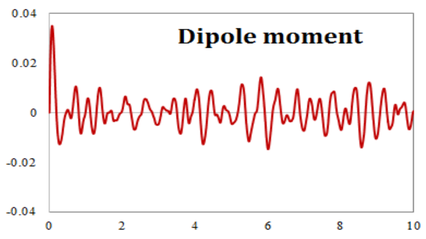
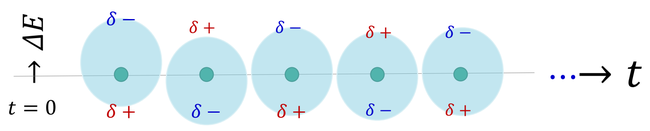


Fig.1 Dynamic dipole moment

2. Dipole moment $\mu(t)$



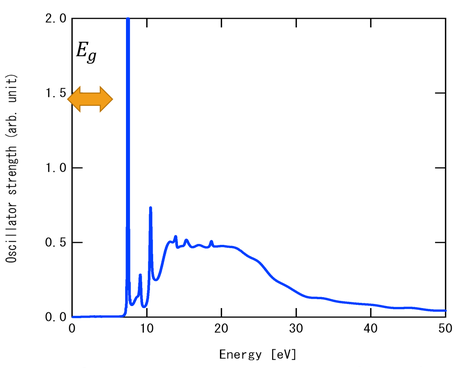


Fig.2 Energy spectrum (C_6H_6)

3. Total oscillator strength/polarizability

$$S_{FT}(\omega) = \frac{2\omega}{\pi}\,\mathrm{Im}\,\alpha(\omega), \alpha(\omega) = \mathcal{F}[\mu(t)\,]$$

Signal Processing of TDDFT time-series data

Fourier Trans.

✓ **FT ⟹ MEM**

III. Procedure of Maximum Entropy Method (Standard MEM)

1. Autocorrelation value of $\mu(n)$

$$C_m = \frac{1}{N}\sum_{n=0}^{N-|m|-1}\mu(n)\,\mu(n+|m|)$$

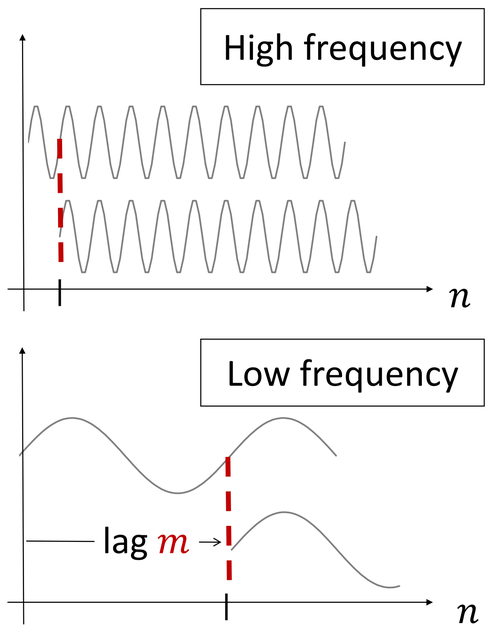


Fig. 3 Illustrated autocorrelation lag

2. Maximum entropy

$$\frac{\partial h}{\partial C_m} = \frac{\partial}{\partial C_m}\left[\int_{-\omega_N}^{\omega_N}\log S(\omega)\,d\omega\right] = 0$$

h ： Information entropy

$$S_{MEM}(\omega) = \frac{\Delta t P_M}{\left|\sum_{m=0}^{M} a_{M,m}\exp[-i\omega m\Delta t]\right|^2}$$

3. Solve Yule-Walker equation

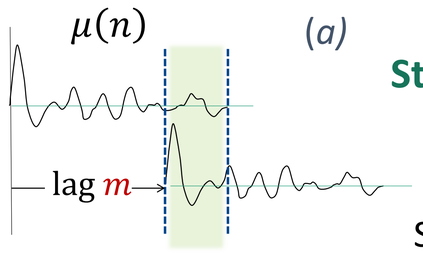
$$\begin{bmatrix} C_0 & C_1 & \cdots & C_M \\ C_1 & C_0 & \cdots & C_{M-1} \\ \vdots & \vdots & \ddots & \vdots \\ C_M & C_{M-1} & \cdots & C_0 \end{bmatrix}\begin{bmatrix} 1 \\ a_{M,1} \\ \vdots \\ a_{M,M} \end{bmatrix} = \begin{bmatrix} P_M \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

$0 \le m \le M$

M ： the maximum lag of C_m

IV. What we innovated

- **Introduction of concatenated data-set made from repeated raw data coupled with phase shift**
- **Effective for the targeted frequency**



Standard MEM provides the signal strength

Low f < High f

Spectrum analysis for optical materials, we focus on **the lower frequency region**

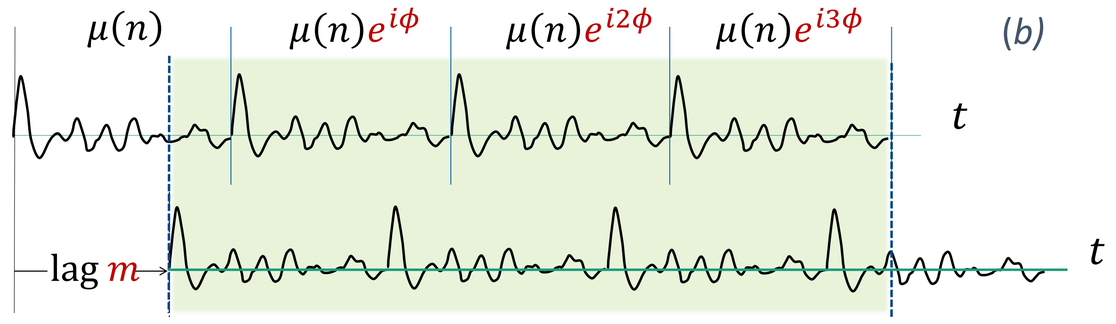


Fig.4. Illustrated autocorrelation with lag m at lower frequency for (*a*) Simple MEM, and for (b) concatenated data-set made from repeated raw data coupled with phase shift.

- **Enhanced autocorrelation for the lower frequency region**
- **Minimization of artificial periodicity due to concatenation by introduction of phase shift for the targeted frequency** [3]

V. Numerical calculations [4]

- Spectral analysis of OLED material such as oligo-fluorene with $n = 8$

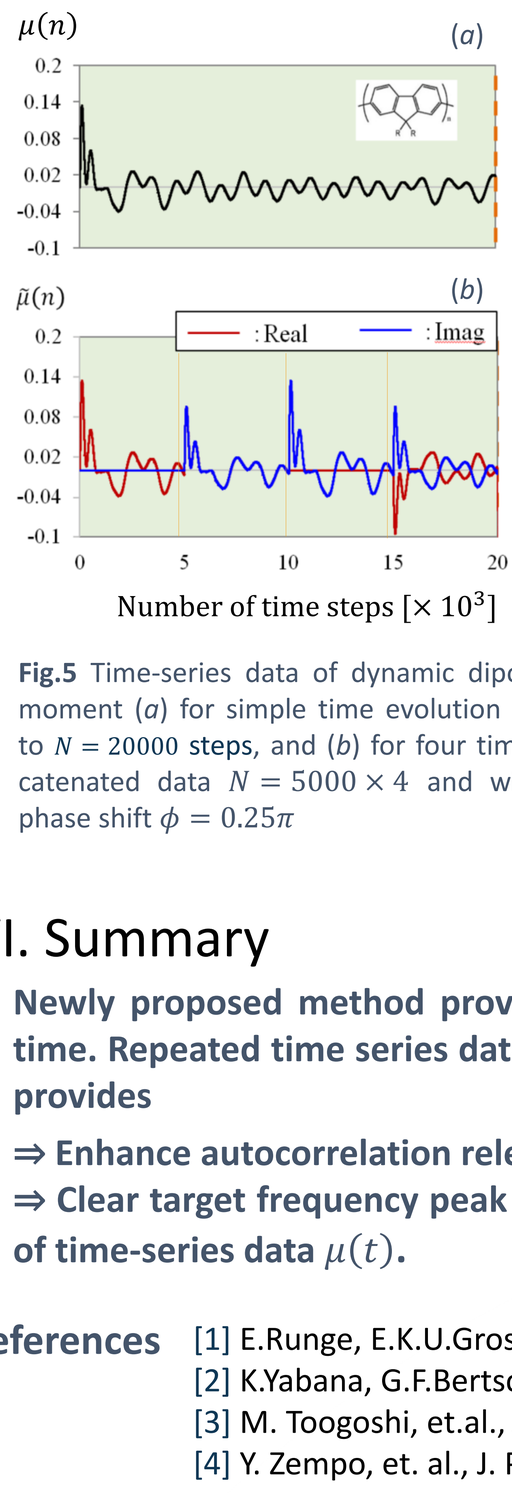


Fig.5 Time-series data of dynamic dipole moment (*a*) for simple time evolution up to $N = 20000$ steps, and (*b*) for four times catenated data $N = 5000 \times 4$ and with phase shift $\phi = 0.25\pi$

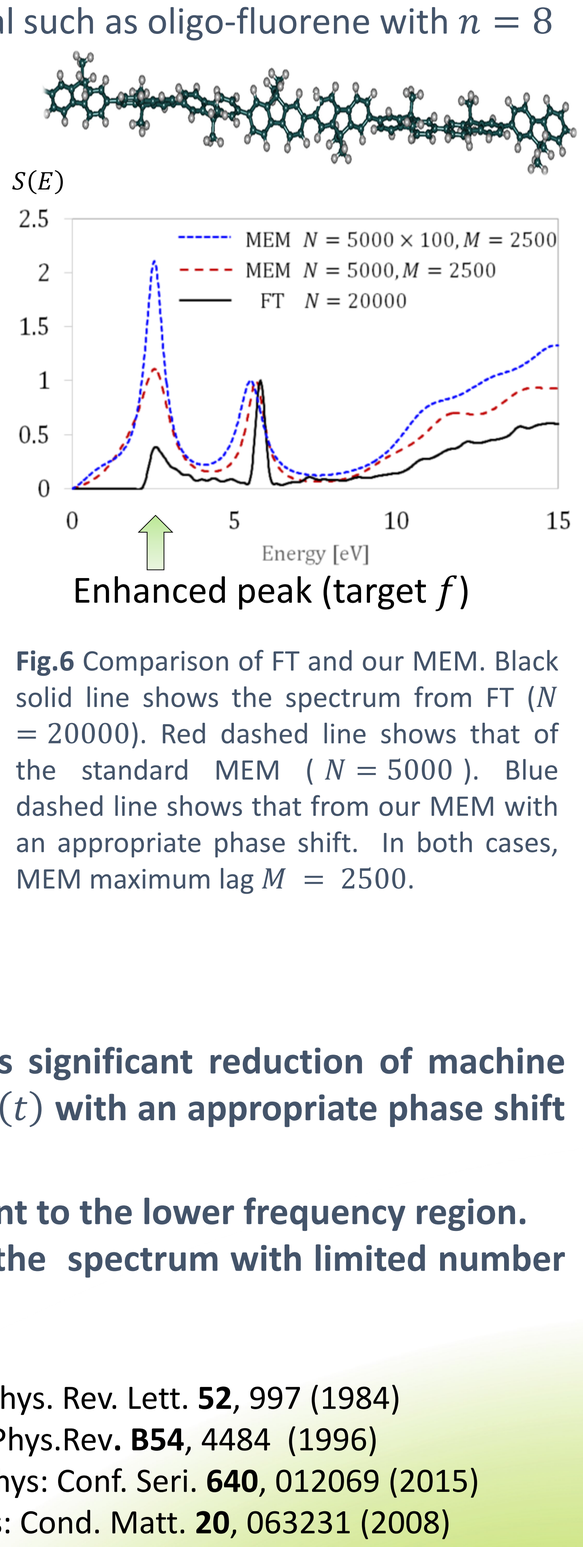


Fig.6 Comparison of FT and our MEM. Black solid line shows the spectrum from FT ($N = 20000$). Red dashed line shows that of the standard MEM ($N = 5000$). Blue dashed line shows that from our MEM with an appropriate phase shift. In both cases, MEM maximum lag $M = 2500$.

VI. Summary

Newly proposed method provides significant reduction of machine time. Repeated time series data $\mu(t)$ with an appropriate phase shift provides

⇒ Enhance autocorrelation relevant to the lower frequency region.

⇒ Clear target frequency peak in the spectrum with limited number of time-series data $\mu(t)$.

References

[1] E.Runge, E.K.U.Gross, Phys. Rev. Lett. **52**, 997 (1984)
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[4] Y. Zempo, et. al., J. Phys: Cond. Matt. **20**, 063231 (2008)