Optical Spectrum Analysis of TDDFT by Maximum Entropy Method

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In computational materials science, meanwhile, many improvements are introduced to DFT as advanced techniques. As one of these improvements, Time Dependent Density Functional Theory (TDDFT) has been a focus of attention recently, which is also introduced in our materials research. In our calculations, the real-time and real-space technique is adopted in solving equation by the finite difference approach. Within the framework of this approach, the wave functions are evolved with the perturbed initial wave function. In the traditional method, the optical strength function is obtained from the frequency Fourier transformation of the dynamic dipole moment.

In frequency domain, however, we can introduce the maximum entropy method (MEM), by which we can obtain a fairly good resolution with a relatively small number of time-series data. This MEM is applied to the spectrum analysis of time-series data of the dipole moment, which is calculated by TDDFT. In our paper, we adopt Burg’s MEM method to compute a best possible spectrum, which is based on the relationship that the known autocorrelation are connected with the power spectrum by a Fourier transform. The major issue of MEM for the spectral estimation is to determine the number of autocorrelation samples. We use Akaike’s final prediction error.

We have applied this MEM to the several spectrum analyses to investigate the calculation efficiency, which is compared to FFT. For demonstration, we calculate the dipole moment of an ethylene molecule up to 20,000 steps with $\Delta t = 4.84 \times 10^{-5}$ fs. The optical strength functions are calculated by FFT and MEM. Both calculations provide a fairly good spectrum results with this time steps. As a result, however, we figure out the advantage of MEM. The 1/4-1/2 series of data are enough for MEM to obtain the similar spectrum by FFT, although the real time evolution of real-time TDDFT consumes a lot of computational resources. In the presentation, we will show the results of MEM applications to several organic materials and those spectra.