Linear response analysis of finite systems: the reasons why "nearsightedness" holds even for finite systems

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Professors Karplus, Warshel and Levitt won the 2013 Novel Prize in chemistry for developing the multiscale models, i.e. quantum mechanics/molecular mechanics (QM/MM) models, for complex chemical systems [1]. This type of approaches relies on the nearsightedness of electronic matter as proposed by Kohn and Prodan [2], which states that the changes of electric potentials at any points that are far enough from a specific point do not affect significantly electronic properties at the point.

We have recently been reexamining the practical aspects of this concept based on linear response function (LRF) analysis with using computational results of simple finite systems [3]. In this study, we examined two types of systems: the first one is the simple model systems such as electrons in square-well potential and electrons in harmonic oscillator potential. The second one is the simple polypeptide systems with using ab initio density functional computational results, which are directly related to the QM/MM applications. The comparison among LRFs ($\delta\rho(\mathbf{r})/\delta v(\mathbf{r'})$) for these two types of systems reveals that the propagations of density deviations ($\delta\rho(\mathbf{r})$) due to virtual perturbations ($\delta v(\mathbf{r'})$) are the results of mainly two type of effects. From the computational results of model systems, the nearsightedness of the systems obviously depends on the number of electrons (N): as N increases, the LRF, $\delta\rho(r)/\delta v(r')$ decays rapidly for the distance, $|r-r'|$. This exemplifies that the principle suggested by Kohn and Prodan [2] holds even for finite systems: the cause of nearsightedness is the destructive interference among single electron density amplitudes. On the other hand, the propagations of the LRFs for polypeptide systems depend rather on the shape of molecular orbitals, and so on the shape of molecular structures. The detailed and numerical analyses of these effects will be presented on that day.

References

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