

# Localized Molecular Orbitals for Large Systems and Their Applications in Excited State Calculations

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## Abstract:

Quantum chemistry methods, as efficient and practical research tools for calculating electronic structures and properties of various systems, have been widely used in the various fields such as chemistry, biology, physics, material science, etc. However, since the computational cost of the conventional quantum chemistry algorithms increases steeply with the system size, it is still difficult to perform accurate quantum chemistry calculations for large systems. In order to solve this problem, many low or even linear scaling algorithms for different theoretical methods have been developed. Among these schemes, local correlation methods have attracted much attention. The localized molecular orbitals (LMOs) play a key role in the local correlation methods. With LMOs, the computational cost of conventional electron correlation methods could be reduced dramatically by neglecting correlation between distant LMOs, because electron correlation is mostly a local phenomenon. On the other hand, excited-state calculations are required to study many important photochemical and photophysical processes. However, excited-state calculations of large systems are even more challenging than the corresponding ground-state calculations. With occupied and virtual LMOs, the working equations of excited-state methods for low-lying electronically excited states can be dramatically simplified without loss of much accuracy. Such LMO-based excited state methods may extend excited-state calculations to very large systems. From the discussions above, one can conclude that the fast and efficient construction of occupied and virtual LMOs for large systems is still a very important subject in quantum chemistry.

Our work includes two parts. First, we have developed a very fast and efficient localization scheme for generating both occupied and virtual regionally localized molecular orbitals (RLMOs). The quality of these RLMOs is very similar to that of the LMOs obtained with conventional localization methods. Second, we also have proposed an efficient localization scheme for constructing RLMOs localized on some fragments for molecular clusters. We then implement the local excitation approximation (LEA) of the TDDFT, TDHF, CIS methods based on RLMOs. The LEA-TDDFT (TDHF, CIS) program is applied to investigate the local  $n$  electronic excitation of acetone in condensed phase. The main contributions and innovations of the present work can be summarized as follows:

(1) We have developed a fast and efficient fragment-based top-down localization scheme to obtain occupied and virtual regionally local molecular orbitals (RLMOs) for large systems. In the scheme, regionally localized molecular orbitals (RLMOs) in many fragments of the target system are

constructed using a fragment-based sequential transformation (ST) strategy based on a series of singular value decomposition (SVD) operations. The locality of RLMOs is quite close to that of LMOs obtained with conventional localization schemes. For several large systems, we demonstrate that this approach is very efficient for computing both occupied and virtual RLMOs.

(2) We have implemented the local excitation approximation (LEA) of time-dependent density functional theory (TDDFT), time-dependent Hartree-Fock (TDHF), and configuration interaction singles (CIS) methods. The main idea of the LEA scheme is that only local electron excitations within a certain active region (called as chromophore) are treated to obtain the excitation energies for locally excited electronic states. We have proposed an efficient localization procedure to obtain regional localized molecular orbitals (RLMOs) localized on the chromophore subunit. The LEA-TDDFT, TDHF, CIS methods have been applied to investigate the solvatochromic shift of the vertical excitation energy of acetone in aqueous solution. To ensure the accuracy of the TDDFT, TDHF and CIS schemes for the studied system, we choose one acetone and six nearest-neighboring waters as the active region for each acetone-water cluster. For acetone in aqueous solution, the LEA-TDDFT calculations on 600 acetone-water configurations (generated from molecular dynamics simulation) suggest that the blueshift in the vertical electronic excitation energy is  $1621 \pm 52$   $\text{cm}^{-1}$ , which is in good agreement with the available experimental blue shift of 1500-1700  $\text{cm}^{-1}$ .

The computational cost of these LEA-based excited-state methods is much less than that of the conventional excited-state methods. The LEA-TDDFT method is expected to become an efficient tool for studying the locally excited states of molecules in condensed phase

#### **References:**

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