

## 論文の内容の要旨

論文題目 : First-principles study of electron correlation in condensed matter with explicitly correlated wave functions  
(露に相関した波動関数による固体の電子相関効果の第一原理的研究)

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First-principles electronic structure calculation is now regarded as an effective and powerful tool for studying condensed-matter physics. Most of the first-principles calculations are carried out using the density functional theory (DFT), which provides the electronic structures with sufficient accuracy and low computational cost in many cases. Despite the great successes of DFT, generally-used approximations have serious drawbacks in accuracy; for example, the band gap is underestimated, the activation energy of the chemical reaction is not correctly reproduced, London dispersion force cannot be described, and strongly correlated systems are not accurately treated. To overcome these problems, wave function theory, in which the many-body wave function is explicitly handled, is a promising way because its accuracy can be improved by refining the many-body wave function in a systematic manner. However, conventional wave function theories are not necessarily suitable for solid-state calculations because the Hartree-Fock (HF) method, the starting point of most of the wave function theories, shows poor accuracy for solid-state calculations, and other wave function theories are very expensive to apply to solid-state calculations.

Transcorrelated (TC) method is one of the promising wave function theories. In the TC method, the many-body wave function is assumed to be a product of a Jastrow factor, which is a symmetric product of a positive two-body function of electron coordinates, and a Slater determinant, which consists of one-electron orbitals. The key idea of the TC method is similarity-transformation of the many-body Hamiltonian by the Jastrow factor, and after this transformation, the TC method can be considered as the HF method applied to the similarity-transformed Hamiltonian because the eigenstate of the similarity-transformed Hamiltonian is assumed to be the Slater determinant. Therefore, one-electron orbitals in the Slater determinant are optimized with a one-body self-consistent-field equation just like the HF method.

The TC method has several advantages for solid-state calculations. First, electron correlation effects are partially retrieved by the Jastrow factor. For example, the screening effect of the electron-electron interaction is partially taken into account through the long-range behavior of the Jastrow factor, which was proved for the uniform electron gas using the random-phase approximation. In addition, short-range correlation when two electrons approach can be retrieved by the Jastrow factor because the Jastrow factor is constructed with the two-body function of electron coordinates. The validity of the TC method owing to these advantages in accuracy is verified in calculations of the uniform electron gas and some simple solids using the TC method. Second, its computational cost is the same order of magnitude as the HF method, i.e.,  $O(N_k^2 N_b^2 N_{pw} \log N_{pw})$  where  $N_k$ ,  $N_b$ , and  $N_{pw}$  are the numbers of the  $k$ -points, bands, and plane waves to expand one-electron orbitals with, respectively, while electron correlation effects are partially taken into account in the TC method as mentioned above. This prominent advantage is due to an efficient algorithm of the TC method developed by the author, which considerably broadened the feasibility of the TC method to solid-state calculations in terms of the computational cost. Third, the band structure and total energy (and Hellmann-Feynman force) can be obtained by the TC method. This advantage is taken for granted in DFT calculations, but not the case for other first-principles methods such as *GW* method, where the Hellmann-Feynman force is not available and so the structural optimization cannot be performed, and quantum Monte Carlo methods, where the band structure is available but computationally demanding to obtain. Moreover, a similarity between the HF and TC methods allows ones to use the TC method as a great replacement of the HF method and apply some sophisticated wave function theories, which conventionally employ the one-electron orbitals and their orbital energies of the HF wave function, to the TC method just in the same way as the HF method. This possibility provides a simple way to improve accuracy of the TC method systematically, which is an important issue for high-accuracy calculations.

In spite of these great advantages, the TC method has a problem to overcome in accuracy. It was verified that the TC method really improves the calculated band structures comparing with the HF method, but not-small errors of the band gaps remain especially for wide-gap insulators. For example, the band gap of lithium fluoride, which is experimentally 14.2 eV, is predicted as 10.5 eV. Also, the errors of the band gaps of other solids are sometimes not so small, e.g., an about 0.5 eV error for the band gap of silicon (about 1.2 eV, experimentally) is observed. Correct band gaps are indispensable, e.g., for treating the impurity problems, for which the relative position of the impurity level to the band structure of bulk solid is important, for studying the chemical

reactions at the solid surfaces, and for predicting the optical response of solids. These issues are of much importance both for theoretical interests and for industrial applications. Moreover, incorrect band gaps sometimes can falsely predict a metal to be an insulator, and vice versa. The advantage of the TC method mentioned above, systematic improvability of accuracy, has, however, not yet been employed to overcome this situation because acceleration of the TC method was carried out very recently and theoretical development of the TC method for solid-state calculations has not sufficiently been investigated yet.

In this thesis, we achieved theoretical improvements of accuracy for the TC method by two ways and applied them to the band structure calculations and excited state calculations of solids (Fig.1). The first way for improving accuracy is to optimize the Jastrow factor based on the random-phase approximation (RPA) and pseudo-variance minimization, and the other one is to apply the second-order Møller-Plesset (MP2) perturbation theory to the biorthogonal TC (BiTC) method. The MP2 perturbation theory combined with the BiTC method was already applied to molecular systems by other researchers, but it has not been

applied to solid-state calculations yet. In these two ways, we improved the Jastrow factor and the Slater determinant in the many-body wave function, respectively. For both methods, we investigated their effects on the calculated band structures, and we found that (i) the long-range behavior of the Jastrow factor, which describes the screening effect of the electron-electron interaction, can be well optimized by our RPA treatment and the band gap of a large-gap insulator is improved (Fig. 2), (ii) the short-range behavior of the Jastrow factor, however, does not affect the calculated band structures so much by using our Jastrow function with limited degrees of freedom, and (iii) the BiTC-MP2 theory yields somewhat unsatisfactory results considering its expensive computational cost: the BiTC method, a starting point of the perturbation, shows good accuracy comparing with the HF method and then the calculated band gaps change very little by the MP2 correction in some cases. These observations suggest that, to obtain more accurate band structures,

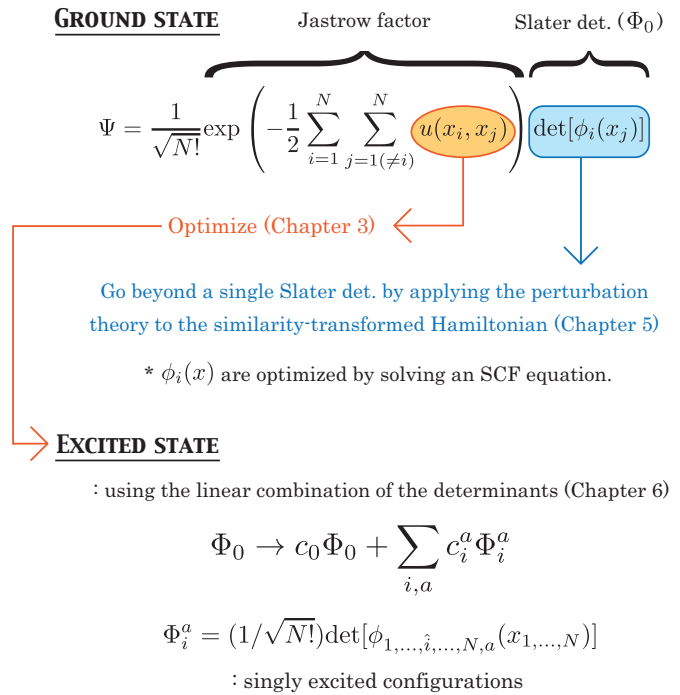


Fig. 1: Graphical abstract of this thesis.

we should describe the screening effect in more rigorous manner than the present treatment with the only one Jastrow parameter. Description of the screening effect can be improved by using more sophisticated Jastrow functions that cannot be written as functions of electron distances or those with more complex long-range behavior, or by combining with more sophisticated wave function theories such as the coupled-cluster theory, which takes account of infinite series of diagrams including the ring diagram. Such treatments will also improve description of the short-range correlation. A study in this direction is an important future issue.

Finally, we proposed a tractable method of excited state calculations by an extension of the TC method and applied it to calculations of the optical absorption spectra of solids using the optimized Jastrow function. We verified that our method predicts the optical absorption spectra with satisfactory accuracy (Fig. 3). Although comparable accuracy can be obtained also by other methods such as *GW*+BSE method, it is important that we can obtain the accurate optical absorption spectra and perform accurate excited state calculations using the TC method, which can provide both the total energy and accurate band structures.

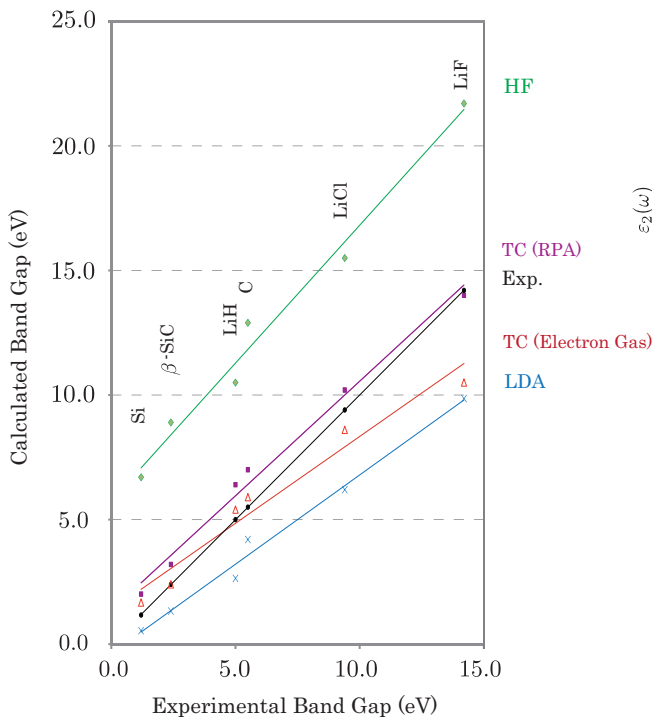


Fig. 2: Band gaps for several solids calculated with each method. Former results of the TC method are denoted as ‘TC (Electron Gas)’, and Jastrow optimization yields ‘TC (RPA)’ results.

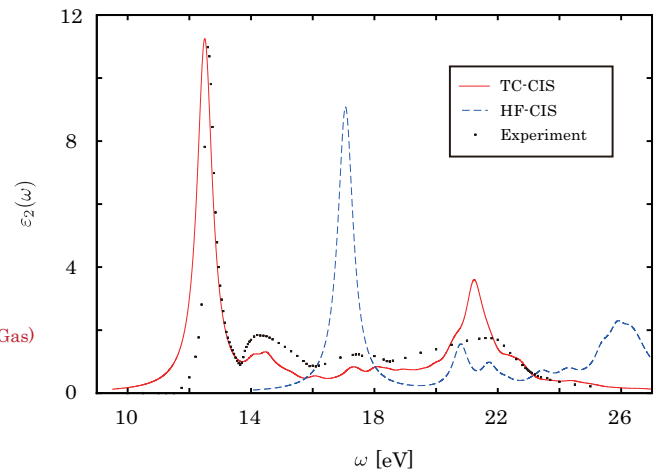


Fig. 3: Calculated optical absorption spectra of solid LiF using the TC-CIS (solid line, our method) and HF-CIS methods.