

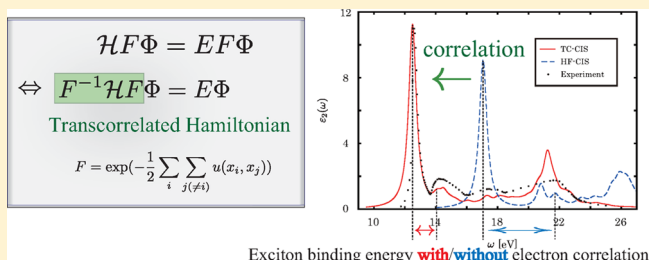
# Optical Absorption Spectra Calculated from a First-Principles Wave Function Theory for Solids: Transcorrelated Method Combined with Configuration Interaction Singles

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**ABSTRACT:** We present a new *ab initio* method for excited-state calculations based on wave function theory: transcorrelated (TC) method combined with configuration interaction singles (CIS). Conventional CIS with the Hartree–Fock wave function, while a popular method for excited-state calculations of molecular systems, cannot describe electron correlation effects, such as the screening effect in solids, resulting in inaccurate results such as overestimation of the band gap and exciton binding energy. Here, we adopt the TC method, which takes electron correlations into account through a similarity transformation of the Hamiltonian using the Jastrow factor, and combine it with the CIS approximation. We calculate the optical absorption spectra of solid LiF and GaAs as a test, and verify that the present method reproduces the spectra more accurately than the conventional HF-CIS. The excitonic effect is well described with our method.



## 1. INTRODUCTION

Accurate descriptions of electron excitations in solids are one of the outstanding challenges in the field of condensed matter physics. In particular, calculations of optical absorption spectra involve theoretical interests of the exciton and industrial applications such as light-emitting diodes and photovoltaic devices. However, accurate *ab initio* calculations of the excited states in solids are known to be very difficult to achieve. Time-dependent density functional theory (TDDFT) is the most popular method to treat the excited state of solids and has succeeded in describing the electronic structure with good accuracy in several cases. However, it is well-known that the simple approximations used in TDDFT such as the adiabatic local density approximation fail to describe the electron–hole interaction in solids, resulting in incorrect structures of optical absorption spectra. In attempting to overcome this problem, much investigation into TDDFT for some simple solids has been actively pursued with success in predicting their optical absorption spectra.<sup>1–3</sup> The GW + Bethe–Salpeter equation (BSE), which is based on the many-body perturbation theory, is also known to be a reliable theory for excited-state calculations.<sup>4–6</sup>

Despite these successes, such calculations based on first-principles wave function theory have been rarely reported. Traditionally, the wave function theory, in which one explicitly assumes a form of the many-body wave function, has established itself as the state-of-the-art theory for molecular systems in the field of quantum chemistry. Also, for ground-state properties in solid-state calculations, diffusion Monte Carlo (DMC) method, one of the wave function theories, is considered to be one of the most accurate theories.<sup>7</sup> DMC has

also been applied in excited-state calculations of for example the quasiparticle gap and optical gap,<sup>8,9</sup> but the whole optical absorption spectrum of the solid is difficult to obtain with DMC. Other wave function theories have been often applied to 1D periodic systems,<sup>10–13</sup> and some early studies of time-dependent Hartree–Fock (HF) theory applied to 3D solids were also reported.<sup>14</sup> Finite cluster approaches have also been applied to periodic systems,<sup>15,16</sup> and recently, configuration interaction singles (CIS) was applied to some simple solids.<sup>17,18</sup> In CIS, one uses the HF wave function as the ground state and expresses the excited states as linear combinations of singly excited Slater determinants. These studies are great steps in the development of the wave function theory for solid-state calculations. However, it is known that the CIS approximation applied to the HF wave function cannot describe the correlation effects at all such as the screening effect of the electron–electron interaction. This is problematic in calculating optical absorption spectra, because the band gap and the exciton binding energy are heavily overestimated.<sup>17</sup> To overcome these difficulties, we developed the TC–CIS method—the transcorrelated (TC) method<sup>19–24</sup> combined with the CIS approximation. The TC method takes the correlation effects into account through the Jastrow factor, hence is expected to be a good candidate to describe well the electronic structure in solids. It is worth noting that the TC method was applied to excited-state calculations of a helium atom yielding successful results.<sup>25</sup> To our knowledge, our calculation of the optical absorption spectrum of solids is the

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first attempt based on the first-principles wave function theory with the Jastrow factor to take account of the correlation effects. In this work, we verify the importance of such correlations for accurate predictions of optical absorption spectra.

## 2. TRANSCORRELATED METHOD COMBINED WITH CONFIGURATION INTERACTION SINGLES

In the TC method, we rewrite a many-body wave function  $\Psi$  in the form  $\Psi = F\Phi$ , where

$$F = \exp\left(-\frac{1}{2} \sum_{i=1}^N \sum_{j=1(\neq i)}^N u(x_i, x_j)\right) \quad (1)$$

is the Jastrow factor, with  $\Phi$  being a many-body function formally defined as  $\Phi_0 = \Psi_0/F$ , and  $x_i$  denotes position  $\mathbf{r}_i$  and spin  $\sigma_i$  of the  $i$ -th electron. The Schrödinger equation for the first-principles Hamiltonian of a many-electron system,

$$\mathcal{H}F\Phi = EF\Phi \quad (2)$$

where

$$\mathcal{H} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(x_i)\right) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1(\neq i)}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (3)$$

is then equivalent to the similarity-transformed eigenvalue equation,

$$\mathcal{H}_{\text{TC}}\Phi = E\Phi \quad (4)$$

where

$$\begin{aligned} \mathcal{H}_{\text{TC}} \equiv F^{-1}\mathcal{H}F = & \mathcal{H} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1(\neq i)}^N (\nabla_i^2 u(x_i, x_j) \\ & - (\nabla_i u(x_i, x_j))^2 + 2\nabla_i u(x_i, x_j) \cdot \nabla_j) \\ & - \frac{1}{2} \sum_{i=1}^N \sum_{j=1(\neq i)}^N \sum_{k=1(\neq i,j)}^N \nabla_i u(x_i, x_j) \cdot \nabla_j u(x_j, x_k) \end{aligned} \quad (5)$$

which is called the TC Hamiltonian. A real part of its expectation value,  $\text{Re}[\langle \Phi | \mathcal{H}_{\text{TC}} | \Phi \rangle / \langle \Phi | \Phi \rangle]$ , gives the total energy. In this study, we use

$$u(x, x') = \frac{A}{|\mathbf{r} - \mathbf{r}'|} \left(1 - \exp\left(-\frac{|\mathbf{r} - \mathbf{r}'|}{C_{\sigma, \sigma'}}\right)\right) \quad (6)$$

where  $A = (1 - 1/\epsilon)^{1/2} \times A_0$  ( $A_0 = (V/4\pi N)^{1/2}$ ,<sup>26</sup>  $\epsilon$  is the dielectric constant calculated with an RPA relation using local density approximation (LDA) orbitals,  $N$  is the number of valence electrons,  $V$  is the volume, and  $C_{\sigma\sigma'} = (2A)^{1/2}$  (spin parallel:  $\sigma = \sigma'$ ),  $(A)^{1/2}$  (spin antiparallel:  $\sigma \neq \sigma'$ ). The long-range behavior of this function is determined so as to reproduce the screened electron–electron interaction in solids as  $1/r \rightarrow 1/\epsilon r$ ,<sup>27</sup> and short-range behavior is determined by imposing the cusp condition.<sup>28</sup> Using this Jastrow function, these electron correlation effects are taken into consideration through the TC Hamiltonian.<sup>27</sup>

For the ground-state calculation,  $\Phi$  is assumed to be a single Slater determinant:

$$\Phi_0 = \frac{1}{\sqrt{N!}} \det[\phi_{1,\dots,N}(x_{1,\dots,N})] \quad (7)$$

and we can optimize one-electron orbitals therein by solving a self-consistent field (SCF) equation similar to the HF method:<sup>22</sup>

$$\begin{aligned} & \left(-\frac{1}{2} \nabla_1^2 + v_{\text{ext}}(x_1)\right) \phi_i(x_1) + \sum_{j=1}^N \int dx_2 \phi_j^*(x_2) \left[\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right. \\ & + \frac{1}{2} (\nabla_1^2 u(x_1, x_2) + \nabla_2^2 u(x_1, x_2) - (\nabla_1 u(x_1, x_2))^2 \\ & - (\nabla_2 u(x_1, x_2))^2 + \nabla_1 u(x_1, x_2) \cdot \nabla_1 + \nabla_2 u(x_1, x_2) \cdot \nabla_2] \\ & \det[\phi_{i,j}(x_{1,2})] - \frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N \int dx_2 dx_3 \phi_j^*(x_2) \phi_k^*(x_3) \\ & [\nabla_1 u(x_1, x_2) \cdot \nabla_1 u(x_1, x_3) + \nabla_2 u(x_2, x_1) \cdot \nabla_2 u(x_2, x_3) \\ & + \nabla_3 u(x_3, x_1) \cdot \nabla_3 u(x_3, x_2)] \det[\phi_{i,j,k}(x_{1,2,3})] \\ & = \sum_{j=1}^N \epsilon_{ij} \phi_j(x_1) \end{aligned} \quad (8)$$

For the excited-state calculation, we assume that  $\Phi$  is a linear combination of determinants,

$$\Phi_{\text{excited}} = c_0 \Phi_0 + \sum_{i,a} c_{i,a} \Phi_i^a \quad (9)$$

where  $\Phi_i^a$  is a singly excited configuration defined as

$$\Phi_i^a \equiv \frac{1}{\sqrt{N!}} \det[\phi_{1,2,\dots,\hat{i},\dots,N-1,N,a}(x_{1,\dots,N})] \quad (10)$$

where an electron of the  $i$ -th occupied state is excited to the  $a$ -th unoccupied state. This approximation where one uses singly excited configurations to represent the excited states is called the CIS, and we call our method the TC–CIS method. Although the band structure is obtained by the ground-state calculation thanks to the Koopmans' theorem,<sup>22</sup> description of the electron–hole interaction requires the explicit treatment of the excited-state wave function where the electron in the conduction bands and hole in the valence bands coexist, and this is a reason why we adopt the CIS approximation to calculate the optical absorption spectra in this study. CIS is usually applied to the HF method (i.e., without the Jastrow factor), and in that case,  $c_0 = 0$  holds because of Hermiticity of the Hamiltonian,<sup>29</sup> which does not hold for our non-Hermitian TC Hamiltonian. In other words, for the TC Hamiltonian,  $\langle \Phi_0 | \mathcal{H}_{\text{TC}} | \Phi_i^a \rangle$  does not equal zero.<sup>27</sup>

Here, we mention physical meaning and verification of our Jastrow–(multi-)Slater-type wave functions. Our Jastrow function eq 6 is rather simple and more complex forms of the Jastrow function seem to be suitable for achieving higher accuracy. Nevertheless, it is known that this simple Jastrow function provides band structures with good accuracy.<sup>27</sup> In addition, the screening effect, which is the most fundamental correlation effect to describe proper electron–hole interaction, is taken into account by our Jastrow function. Therefore, in this study, we adopt this simple Jastrow function and consider that the ground state is well approximated by the Jastrow–Slater-type wave function. In other words, the many-body Hamiltonian similarity-transformed by the Jastrow factor provides the proper effective interaction for quasi-particles that construct the Slater determinant. In this situation, our CIS approximation is a reasonable and practical way to describe the excited states. Note that the Jastrow factors of the Jastrow–

(multi-)Slater-type wave functions are generally different between the ground and excited states,<sup>25</sup> but here, we use the same one because the conditions imposed on our Jastrow function, that is, the RPA and cusp conditions, should be satisfied as is for the excited states.

The TC-CIS calculation is performed as follows: (i) we obtain orthonormalized one-electron orbitals and their orbital energies by solving the SCF equation (eq 8) for the ground state, (ii) CI-matrix elements for  $\Phi_0$  and  $\Phi_i^a$  (e.g.,  $\langle \Phi_i^a | \mathcal{H}_{TC} | \Phi_j^b \rangle$ ) are calculated, (iii) the CI-matrix is diagonalized and coefficients ( $c_0$  and  $c_{i,a}$  for each  $\Phi_{\text{excited}}$ ) are obtained. We also calculate the optical absorption spectrum; the method will be described below.

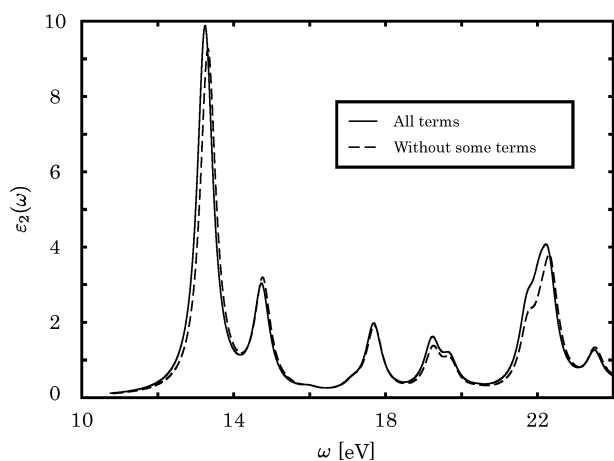
The calculation of the CI-matrix elements appears to be computationally expensive because its cost scales as  $O(N_k^3)$  owing to the three-body terms in the TC Hamiltonian; here,  $N_k$  is the number of  $k$ -points. However, many parts of the three-body terms can be calculated at  $O(N_k^2)$  cost using a technique used in the ground-state calculation,<sup>30</sup> and we verified that the remaining few terms that require  $O(N_k^3)$  computational cost, which have forms of

$$-\sum_{k=1}^N \int dx_1 dx_2 dx_3 \phi_a^*(x_3) \phi_j^*(x_2) \phi_k^*(x_1) \nabla_1 u(x_1, x_2) \cdot \nabla_1 u(x_1, x_3) \phi_b(x_1) \phi_k(x_2) \phi_l(x_3) \quad (11)$$

and

$$-\sum_{k=1}^N \int dx_1 dx_2 dx_3 \phi_a^*(x_3) \phi_j^*(x_2) \phi_k^*(x_1) \nabla_2 u(x_2, x_1) \cdot \nabla_2 u(x_2, x_3) \phi_k(x_1) \phi_l(x_2) \phi_b(x_3) \quad (12)$$

in  $\langle \Phi_i^a | \mathcal{H}_{TC} | \Phi_j^b \rangle$ , yield small contributions to the optical absorption spectra for the materials focused on in this work (LiF and GaAs). Figure 1 shows calculated optical absorption spectra of solid LiF using a  $4 \times 4 \times 4$   $k$ -point mesh considering all terms in the TC Hamiltonian or neglecting expensive terms presented in eqs 11 and 12 that require  $O(N_k^3)$  computational cost. We see that the neglected terms have little effect on the



**Figure 1.** Calculated optical absorption spectra of LiF using a  $4 \times 4 \times 4$   $k$ -point mesh considering all terms (solid line) or neglecting some portion of the three-body terms (dashed line) in the TC Hamiltonian.

calculated absorption spectrum of LiF, and the same also holds for GaAs. Henceforth, we shall neglect these expensive terms in the CIS calculations. Of course, two kinds of three-body terms we shall neglect here are a small portion of the whole terms: all the one- and two-body terms, and 18 kinds of three-body terms, but it is not easy to justify our approximation from a theoretical aspect by providing some physical meaning of these terms. However, it seems to be natural to expect that three-body terms that have the same indices of the coordinates between  $\phi_k$  and  $\phi_k^*$ , for example,

$$-\sum_{k=1}^N \int dx_1 dx_2 dx_3 \phi_a^*(x_1) \phi_j^*(x_2) \phi_k^*(x_3) \nabla_3 u(x_3, x_1) \cdot \nabla_3 u(x_3, x_2) \phi_i(x_1) \phi_b(x_2) \phi_k(x_3) \quad (13)$$

play a more dominant role than the other three-body terms because we can perform summation over  $k$  in eq 13 as  $\sum_{k=1}^N |\phi_k(x_3)|^2$  without any cancellation caused by phases of one-electron orbitals. This aspect also relates to that some of the three-body terms that have the same indices of the coordinates between  $\phi_k$  and  $\phi_k^*$  describe the screening effect for some two-body terms, for example,

$$\int dx_1 dx_2 \phi_a^*(x_1) \phi_j^*(x_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_i(x_1) \phi_b(x_2) \quad (14)$$

which can be easily verified in the same way as presented in our previous paper,<sup>27</sup> though other three-body terms such as eqs 11 and 12 do not have such corresponding two-body terms.

We also face another difficulty in calculating the optical absorption spectrum. The optical absorption spectrum is obtained from the imaginary part of the dielectric function,  $\epsilon_2(\omega)$ , which is

$$\epsilon_2(\omega) = \left( \frac{2\pi}{\omega} \right)^2 \sum_n \frac{|\langle F\Phi_0 | \mathbf{e}_\lambda \cdot \nabla | F\Phi_n \rangle|^2}{\langle F\Phi_0 | F\Phi_0 \rangle \langle F\Phi_n | F\Phi_n \rangle} \times \delta(\omega - (E_n - E_0)) \quad (15)$$

where  $n$  denotes an index of an excited state, and  $\mathbf{e}_\lambda$  a polarization vector of the photon. However, evaluation of this quantity requires a  $3N$ -dimensional integration, which is computationally quite expensive. To avoid doing this integration for this study, we calculate

$$\left( \frac{2\pi}{\omega} \right)^2 \sum_n \frac{|\langle F^{-1}\Phi_0 | \mathbf{e}_\lambda \times \nabla | F\Phi_n \rangle|^2}{\langle \Phi_0 | \Phi_0 \rangle \langle \Phi_n | \Phi_n \rangle} \delta(\omega - (E_n - E_0)) \quad (16)$$

instead of eq 15. The relation between these two quantities is described as follows: first,

$$\begin{aligned} & \frac{|\langle F^{-1}\Phi_0 | \mathbf{e}_\lambda \times \nabla | F\Phi_n \rangle|^2}{\langle \Phi_0 | \Phi_0 \rangle \langle \Phi_n | \Phi_n \rangle} \\ &= \frac{\left| \langle F^{-1}\Phi_0 | \left( \sum_j \frac{|F\Phi_j\rangle \langle F\Phi_j|}{\langle F\Phi_j | F\Phi_j \rangle} \right) \mathbf{e}_l \times \nabla | F\Phi_n \rangle \right|^2}{\langle \Phi_0 | \Phi_0 \rangle \langle \Phi_n | \Phi_n \rangle} \end{aligned} \quad (17)$$

holds where  $j$  is summed over all eigenstates of  $\mathcal{H}$ . Next, we suppose  $|\langle \Phi_0 | \Phi_j \rangle| \ll \langle \Phi_0 | \Phi_0 \rangle$  for  $j \neq 0$ , and hence, we only consider the  $j = 0$  term in eq 17. This yields

$$\text{eq 17} \simeq \frac{|\langle F\Phi_0 | \mathbf{e}_\lambda \times \nabla | F\Phi_n \rangle|^2}{\langle F\Phi_0 | F\Phi_0 \rangle \langle F\Phi_n | F\Phi_n \rangle} \frac{\langle \Phi_0 | \Phi_0 \rangle \langle F\Phi_n | F\Phi_n \rangle}{\langle F\Phi_0 | F\Phi_0 \rangle \langle \Phi_n | \Phi_n \rangle} \quad (18)$$

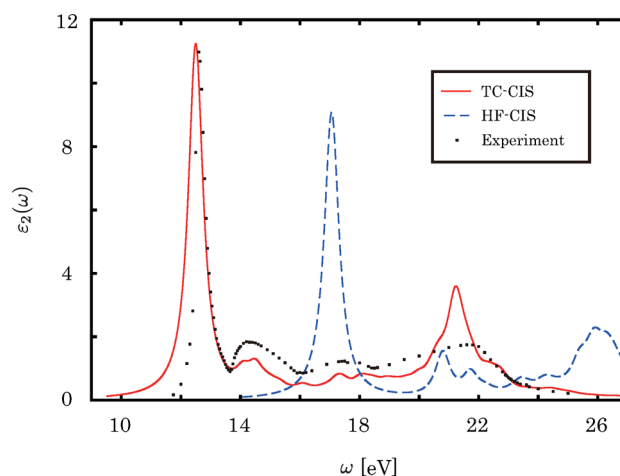
In addition, assuming  $\langle F\Phi_0|F\Phi_0\rangle/\langle\Phi_0|\Phi_0\rangle \simeq \langle F\Phi_n|F\Phi_n\rangle/\langle\Phi_n|\Phi_n\rangle$ , the latter factor in eq 18 becomes 1, and therefore, we find that eqs 15 and 16 are approximately the same. The approximations we used here are not easily validated, but we shall see that the obtained spectra possess sufficient accuracy for a quantitative discussion. Equation 16 involves  $F^{-1}\nabla F = \nabla - \sum_{i<j}(\nabla_i + \nabla_j)u(\mathbf{r}_i, \mathbf{r}_j)$ , which is easy to evaluate, and in particular, when we use the Jastrow function satisfying  $u(\mathbf{r}_i, \mathbf{r}_j) = u(\mathbf{r}_i - \mathbf{r}_j)$ ,  $F^{-1}\nabla F = \nabla$  holds.

We can also apply the CIS approximation to a biorthogonal formulation<sup>31</sup> of the TC method. In the biorthogonal TC method, one uses the left Slater determinant  $X$  that consists of one-electron orbitals  $\chi(x)$  satisfying a biorthogonality condition  $\langle\chi_i|\phi_j\rangle = \delta_{ij}$ . When one constructs biorthogonal TC–CIS formulation, there are some small modifications: (i) eq 9 does not have the  $c_0\Phi_0$  term owing to the Brillouin's theorem,<sup>31</sup> and (ii)  $\Phi_0$  and  $\Phi_n$  on the “bra”-side in eq 16 are replaced with the left determinants  $X_0$  and  $X_n$  whereas the complete set inserted in eq 17 should be unchanged. For the latter point (ii), one might consider that the approximation for evaluating the dielectric function can be more easily validated if we consider  $F^{-1}X$  to be a left eigenstate of the Hamiltonian. However, because the Jastrow factor are inversely multiplied here,  $F^{-1}X$  should be a poor estimate of the left eigenstate of the Hamiltonian and rather be considered as a biorthogonal projector corresponding to  $F\Phi$ . Therefore, also in the biorthogonal formulation, the same explanation as presented above is required for the approximation for calculating the dielectric function.

### 3. RESULTS AND DISCUSSION

LDA<sup>32</sup> calculations were performed with TAPP code<sup>33,34</sup> using a plane-wave basis, and the HF and TC calculations with TC++ code.<sup>23,30</sup> One-electron orbitals used in the HF and TC methods are expanded as linear combinations of LDA orbitals. Convergence of our results was achieved with respect to the number of LDA orbitals. Nonlocal norm-conserving pseudopotentials generated by the method developed by Troullier and Martins<sup>35</sup> were used for the LDA, HF, and TC calculations. For the HF and TC calculations, singularities in the electron–electron Coulomb interaction and the Jastrow function in  $k$ -space were handled following a method proposed by Gygi and Baldereschi,<sup>36</sup> where we used an auxiliary function of the same form as that proposed by Massidda et al.<sup>37</sup> Experimental lattice constants (7.59 Bohr for LiF<sup>38</sup> and 10.68 Bohr for GaAs<sup>39</sup>) are used. The values of  $A/A_0$  are 0.7264 for LiF and 0.9596 for GaAs. It is noteworthy that the HF-CIS results we shall present in this section correspond to the TC-CIS results using  $A/A_0 = 0$  (i.e.,  $F = 1$ ).

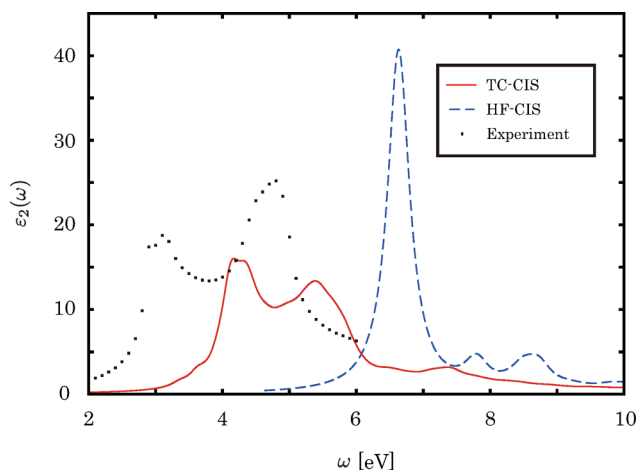
First, we calculated the optical absorption spectrum of solid LiF, which is known for its very strongly bound exciton. Figure 2 presents the optical absorption spectra calculated using the TC-CIS and HF-CIS methods with a  $10 \times 10 \times 10$   $k$ -point mesh, 81 Ry cutoff energy for plane waves, and 100 LDA orbitals for the expansion of the one-electron orbitals for both the HF and TC methods. Three valence bands and six conduction bands from the Fermi energy are used for electron excitation. We can see that the overall structure of the experimental spectrum is well reproduced with both TC-CIS and HF-CIS. However, HF-CIS has two problems. First, the band gap is heavily overestimated, and therefore, the spectrum is shifted to the high-energy region. Second, the exciton binding energy for HF-CIS is over 4 eV, which is much larger than the



**Figure 2.** Calculated optical absorption spectra of LiF using TC-CIS (solid line) and HF-CIS (dashed line). Broadening is performed using the Lorentz function  $f(x; x_0, \gamma) = \gamma/\pi((x - x_0)^2 + \gamma^2)$  with  $\gamma = 0.3$  eV. Experimental data<sup>41</sup> are represented by dots.

experimental value, from 1.4 to 1.9 eV.<sup>40</sup> Recall that the binding energy is defined as the difference between the energy corresponding to the sharp excitonic peak (see Figure 2) and the direct band gap at the  $\Gamma$  point obtained with the ground-state calculation. This large deviation reflects the fact that HF-CIS cannot describe the screening effect of the electron–electron interaction, yielding heavily overbinding exciton. TC-CIS notably overcomes these problems and yields a surprisingly accurate spectrum. The band gap is correctly reproduced and the exciton binding energy is about 1.5 eV, which falls within the range of the experimental values. Our simple Jastrow factor enables an accurate description of the electronic structure in solids, including the exciton.

Next, we calculated the optical absorption spectra of solid GaAs, presented in Figure 3. We used a  $10 \times 10 \times 10$   $k$ -point mesh, 36 Ry cutoff energy for plane waves, 80 LDA orbitals in the expansion of the one-electron orbitals, and three valence bands and six conduction bands from the Fermi energy for electron excitation. For this material, we shifted the  $k$ -point mesh where electron excitations occur for  $-0.01\mathbf{b}_1 - 0.02\mathbf{b}_2 +$



**Figure 3.** Calculated optical absorption spectra of GaAs using the TC-CIS (solid line) and HF-CIS (dashed line). Broadening is performed using the Lorentz function with  $\gamma = 0.15$  and 0.2 eV for TC-CIS and HF-CIS, respectively. Experimental data<sup>46</sup> are represented by dots.



0.03b<sub>3</sub> with {b<sub>1</sub>, b<sub>2</sub>, b<sub>3</sub>} being the basic reciprocal-lattice vectors. The idea to use a shifted grid to achieve a good spectral resolution was originally proposed by Rohlfling and Louie<sup>42</sup> and using a constant shift follows its use in ref 43. In using HF-CIS, there is a large discrepancy between the experimental data and the calculated spectrum, where we see a large shift of the whole spectrum to the high-energy region and a wrong strongly bound excitonic peak with very strong intensity. The direct band gap at the  $\Gamma$  point calculated with the HF method is 7.8 eV, and hence, the calculated exciton binding energy is about 1 eV, whereas experimentally it is a few meV with a very small intensity.<sup>44</sup> These trends in the results from HF-CIS is similar to those of LiF. Although the spectrum calculated with TC-CIS is also shifted to the high-energy region through the overestimation of the band gap in the ground-state calculation and shows incorrect relative heights of the characteristic two peaks, those two peaks are reproduced in contrast to the HF-CIS spectrum. (cf., the band gap at the  $\Gamma$  point of GaAs is 1.4 eV in experiment<sup>45</sup> and 3.1 eV calculated with the TC method.) To obtain a more accurate spectrum, an accurate prediction of the band structure, which determines the joint density of states and effective masses of electrons and holes, in the ground state calculation is indispensable. Other possible reasons of disagreement are (i) inaccuracy of the electron–hole interaction while the screened electron–hole Coulomb interaction at a large distance is considered to be well represented by our Jastrow factor using the dielectric constant, or (ii) the approximation presented in eqs 17 and 18 though it is difficult to evaluate the effect of this approximation. For improving the accuracy of the band structure or the electron–hole interaction, the correlation effects not captured with our simple treatment will be necessary by means of either a much complex Jastrow factor or a combination of the TC method with more elaborate post-HF theories.

Interestingly, although our TC-CIS method is an apparently different method from the well-known GW+BSE method, there are some interesting similarities. The screening effect of the electron–electron interaction is described by the Jastrow factor in the TC method, and by the screened interaction  $W$  in GW; also, the CIS approximation is usually used also in GW+BSE calculations as the Tamm–Dancoff approximation. Some examples of the differences between the two methods are the following: (i) the screening effect is described by only one parameter in our Jastrow factor, which is too simple compared with the way screening is considered in GW+BSE, and (ii) the cusp condition is taken into account by the Jastrow factor in TC-CIS whereas it is difficult to do so in GW+BSE. Such differences can lead to the differences observed in the calculated spectra (cf., ref 6).

#### 4. CONCLUDING REMARKS

In conclusion, we developed a new *ab initio* method based on the wave function theory, namely the TC-CIS method, for excited-state calculations and obtained the optical absorption spectra of some simple solids. The TC-CIS method well reproduced the experimental spectra, both for the sharp excitonic peak of LiF and for the entire structure of both LiF and GaAs. Although similar or sometimes better agreement with experiment can be obtained using GW+BSE or TDDFT with long-range kernels, an accurate description of the spectra based on the first-principles wave function theory, that is, using explicit many-body wave functions, is helpful to understand how we describe electron correlations by means of such wave

functions, and will be the basis for systematic improvements in the spectral calculations. The success of our rather simple formalism suggests great potential of the wave function theory for excited-state calculations of solids. In addition, we believe that some approximation techniques we developed in this work are valuable also for other wave function theories when obtaining the optical absorption spectra.

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##### Notes

The authors declare no competing financial interest.

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