

All-electron first-principles $GW +$ Bethe-Salpeter calculation for optical absorption spectra of sodium clusters

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The optical absorption spectra of sodium clusters (Na_{2n} , $n \leq 4$) are calculated by using an all-electron first-principles $GW +$ Bethe-Salpeter method with the mixed-basis approach within the Tamm-Dancoff approximation. In these small systems, the excitonic effect strongly affects the optical properties due to the confinement of exciton in the small system size. The present state-of-the-art method treats the electron-hole two-particle Green's function by incorporating the ladder diagrams up to the infinite order and therefore takes into account the excitonic effect in a good approximation. We check the accuracy of the present method by comparing the resulting spectra with experiments. In addition, the effect of delocalization in particular in the lowest unoccupied molecular orbital in the GW quasiparticle wave function is also discussed by re-diagonalizing the Dyson equation.

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Optical absorption spectra are one of the most important information of the standard optical properties of condensed materials, and can be therefore a fingerprint when one studies those properties. Until now, several experimental measurements of optical absorption spectra have been done for various materials from molecules and clusters (isolated systems) to bulk crystals (extended systems). Nevertheless, in a theoretical viewpoint, reliable methods of calculating optical absorption spectra are still very limited because of the two main problems we should overcome. One is the so-called band-gap problem that the conventional methods based on the density functional theory (DFT) using the local density approximation (LDA) or generalized gradient approximation (GGA) cannot give the quasiparticle energy spectra. The other is difficult to include in the excitonic effect, which is the Coulomb interaction between an electron lifted up to the conduction band and a hole generated in the valence band. To overcome these two problems, it is required to go beyond the framework of the DFT and to introduce an electron-hole two-particle picture. One method capable of estimating the optical absorption spectra is a linear response theory using the random phase approximation (RPA) within the time-dependent density functional theory; in which, in many cases, the LDA is used for the exchange-correlation kernel f_{xc} [1–4]. However, the agreement with the experimental spectra is not very satisfactory and gets worse as the system size increases because of the lack of long-range interaction due to the use of the LDA [5].

In the last few decades, the first-principles Green's function methods based on the many-body perturbation theory have been developed as a new method capable of treating the excited states of real materials with a high accuracy and efficiency. The $GW +$ Bethe-Salpeter equation (BSE) method [5–9], in which the electron-hole two-particle Green's function is calculated by means of the ladder diagrams up to the infinite order within the GW approximation (GWA), enables us to accurately calculate the optical absorption spectra that take into account the excitonic effect. Until now, the $GW +$ BSE method has

been successfully applied to noble gas atoms, polymers, semiconductors, and insulators to calculate their optical absorption spectra. However, in contrast to the great success in the case of bulk systems, discrepancies with experimental spectra have been pointed out for isolated systems, in particular for small-sized systems [5,7].

In this Brief Report, we apply an all-electron mixed basis $GW +$ BSE method [9] to the calculation of the optical absorption spectra of Na_{2n} clusters ($n \leq 4$) and compare them with the preexisting experimental data. So far, Na_2 and Na_4 have been treated, respectively, in Refs. [6,8,9]. In the present work, we also calculate the optical absorption spectra with the use of the GW quasiparticle wave function by re-diagonalizing the Dyson equation and show that the discrepancy of the BSE results with the experiments is caused, at least partly, by the inaccuracy of the LDA wave function at the empty levels below the vacuum level.

Here we briefly explain the $GW +$ Bethe-Salpeter formalism. The present calculation is established mainly by the following two stages. In the first stage, the accurate one-particle quasiparticle energy spectra including the first ionization potential and the electron affinity are estimated in the GW calculation [10–15]. In the present work, to obtain the GW wave functions, we also perform re-diagonalization of the Dyson equation by considering the off-diagonal elements, $\langle i | \Sigma^{GW}(\epsilon) - \mu_{xc} | j \rangle$, where $\Sigma^{GW}(\epsilon)$ is the self-energy operator and μ_{xc} is the LDA exchange-correlation potential.

In the second stage, the Coulomb interaction between the electron launched to the empty state and the hole generated in the occupied state is taken into account by considering the effective two-particle Hamiltonian and solving its eigenvalue problem within the Tamm-Dancoff approximation [16], which vanishes the coupling part bridging between the resonant part and antiresonant part. Then the kernel in the BSE is expressed as $\Xi \simeq -U^{\text{ex}} + W^{\text{d}}$, where U is a bare Coulomb interaction corresponding to an exchange term which comes from the Hartree operator and W is a dynamically screened Coulomb

interaction corresponding to a direct term which comes from the GW self-energy operator (note that a higher-order exchange term $G \frac{\partial W}{\partial G}$ is neglected because it is small [9,17]). The other details of the present formulation are the same as those given in Refs. [7,8] although they used pseudopotentials.

The present excited-state calculations are performed in terms of an all-electron mixed-basis approach in which a wave function is expanded as a linear combination of the plane waves (PW's) and the atomic orbitals (AO's) constructed with cubic harmonics and numerical radial functions in a logarithmic radial mesh. Due to the use of both of the AO's describing the localized states and the PW's describing the extended states, we can efficiently and accurately describe the whole states with the small basis set (note that, in this study, especially using the PW's is a significant point because the perturbation theory requires accurately treating the free electron states above the vacuum levels in their summation for the empty states). The present calculations are all done by using the supercell with a cubic edge of 31.9 Å (the same cell size as that used in our previous paper [15]) and also the spherical-cut technique to eliminate the interaction with the cluster located in the nearest-neighbor cells [8,18] (we checked the supercell size dependence carefully and found that this cell size of 31.9 Å is already large enough to regard that the clusters treated here are almost *isolated*). We also use 80 empty levels corresponding to 2.5 eV for the summation of the empty states in the BSE to get good convergence. The other computational condition we use in this calculation is the same as in Ref. [15].

The computational time required for Na₈ is about 207 s to calculate both the polarizability function within the random phase approximation and the corresponding inverse of the dielectric function, and about 22 s for computing each expectation value of the GW self-energy operator, $\langle i | \Sigma^{GW}(\epsilon) | i \rangle$, by using 1 node on the HITACHI SR11000/K1 supercomputer whose processing speed is 135 GFLOPS/node.

Table I shows the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of Na clusters calculated with the LDA and the GWA as well as the available experimental energy gap, that is, the difference between the first ionization potential [19] and the electron affinity [20] measured by (inverse) photoemission experiments. As is well known, the LDA underestimates the HOMO-LUMO gap by a few electron volts. In some cases, however, it might be closer to the optical gap measured by photoabsorption experiments rather than the

HOMO-LUMO gap because of the double mistake of the LDA. That is, although the LDA Kohn-Sham orbital energy estimates neither the single quasiparticle energy spectra nor the exciton binding energy, which plays an important role in determining the optical absorption spectra, these mistakes of the LDA tend to cancel each other. Therefore, only when the cancellation becomes (almost) perfect, the LDA gap is close to the optical gap accidentally.

On the other hand, the GW calculation significantly improves the underestimated LDA HOMO-LUMO gap. The remaining discrepancy with the experiment is only about 0.1 eV (see Table I). The effect of the re-diagonalization of the Dyson equation in the resulting HOMO-LUMO gap is small. For Na₆ and Na₈, we cannot compare the GW results in terms of the HOMO-LUMO gap because there is no experimental electron affinity. However, the GW quasiparticle energy agrees with the experimental first ionization potential very well (we do not list it here; the reader may refer to our previous paper [15]). In spite of the great success of calculating the single quasiparticle energy, the GWA is still not enough to calculate the optical absorption spectra because of the lack of the account of the excitonic effect. However, the GWA is a good starting point for more complicated excited-state calculations. And in the present work, it is used as an input for constructing the BSE.

Before calculating the optical absorption spectra of Na clusters, we discuss the matrix elements of the bare and dynamically screened Coulomb interactions between the HOMO and LUMO levels, which usually carry the largest contribution to determine the optical absorption spectra. The lowest exciton binding energy (BE) is, in the present method, composed of the exchange term $U_{o',o';e,e}^{\text{ex}}$ with spin factor 2 for the singlet exciton and the direct term $W_{e,o';e',o'}^d$, which is additionally divided into the bare Coulomb part $U_{e,o';e',o'}^d$ and the rest describing the effect of screening $Z_{e,o';e',o'}^d$, where the index $e(e')$ is the LUMO level and $o(o')$ is the HOMO level. Table II lists the exciton BE of Na clusters and the explicit value of each term (matrix element) contributing to it. The bare Coulomb interaction, both in the exchange and direct terms, shows a clear tendency that the interaction becomes smaller as the cluster size increases. This tendency seems reasonable because the smaller the cluster, the bigger the effect of the confinement of the electron-hole pair (exciton) into the small space. However, the cluster-size dependence of these bare Coulomb interactions consequently disappears in the lowest exciton BE as listed in Table II because the screening $Z_{e,o';e',o'}^d$ in the direct term does not behave in this way; it is negatively larger for Na₄ and Na₆. For all clusters, the exciton BE is larger

TABLE I. HOMO-LUMO gap calculated by the LDA and the GWA (in eV). Also the experimental values, which are estimated from a difference between the experimental first ionization potential [19] and the experimental electron affinity [20], are listed for comparison. The values in the parentheses are the GW gap estimated after the re-diagonalization of the Dyson equation.

	LDA gap	GW gap	Expt.
Na ₂	1.23	4.35(4.28)	4.39
Na ₄	0.58	3.24(3.23)	3.13
Na ₆	1.11	3.35(3.34)	–
Na ₈	1.13	3.25(3.33)	–

TABLE II. The lowest exciton binding energy (BE), which is estimated by $U_{e,o';e',o'}^d + Z_{e,o';e',o'}^d - 2 \times U_{o',o';e,e}^{\text{ex}}$, and each term contributing it (in eV).

	$U_{o',o';e,e}^{\text{ex}}$	$U_{e,o';e',o'}^d$	$Z_{e,o';e',o'}^d$	Exciton BE
Na ₂	1.09	4.53	–0.24	2.12
Na ₄	0.84	4.45	–0.61	2.19
Na ₆	0.58	3.94	–0.64	2.13
Na ₈	0.40	3.79	–0.53	2.47

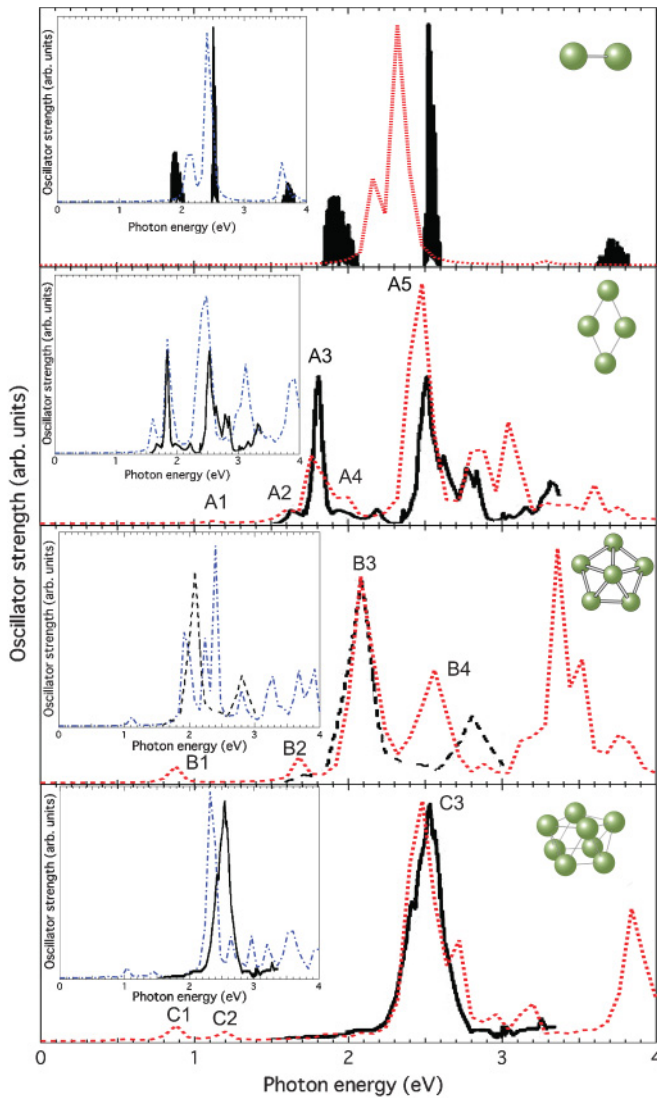


FIG. 1. (Color online) Optical absorption spectra of Na clusters. The dotted line is the calculated $GW + BSE$ spectra using the LDA wave functions and the solid line is the experiment [21–23]. Inset is the $GW + BSE$ spectra using the GWA wave functions after rediagonalization.

than 2 eV and not neglectable in the calculation of the optical absorption spectra.

Next we solve the BSE and calculate the optical absorption spectra including the excitonic effect. Figure 1 shows the calculated spectra of Na_2 together with the experimental spectra [21] for comparison. The dotted (red) line is the calculated spectra where the LDA wave function is used through the calculation. Up to a photon energy range of 4.0 eV, the experimental spectra (black) have well-separated three peaks around 1.9, 2.5, and 3.7 eV. In addition, theoretical results have three peaks around 2.1, 2.3, and 3.3 eV. The agreement with the experiment is fairly good, but not perfect in both the peak position and relative peak height. These small discrepancies with the experiment might be caused by the use of the LDA wave function. As already reported by Rohlfing and Louie in Ref. [7], the LDA wave function at an empty state tends to localize more than the *exact* one, in particular

for the small-sized systems of which the anion is unstable, and consequently the use of the LDA wave functions causes the overestimation of the exciton BE. Therefore we construct the GW quasiparticle wave functions by rediagonalizing the Dyson equation and construct the BSE by using them. A remarkable change from the dotted (red) line occurs when we solve this renormalized BSE as shown in the inset in Fig. 1; the first and second peaks clearly separate, and the third peak redshifts by about 0.3 eV and its oscillator strength becomes stronger. The agreement of the peak position with the experiment becomes better. Here, it is interesting to note that, for example, in the LDA and GWA energies, which do not involve the exciton effect, the first peak could appear at 1.2 and 4.4 eV, respectively, which are far off the optical gap of ~ 2.0 eV.

The optical absorption spectra of Na_4 is a little more complicated than those of Na_2 because the single quasiparticle energy spectra are already complicated. So we labeled the remarkable five peaks found in the present result as A1, A2, A3, A4, and A5 from the low-energy side to the high-energy side (see Fig. 1). According to the GW HOMO-LUMO gap and the lowest exciton BE we discussed in the previous section, although the first peak corresponding to the HOMO-LUMO transition including the excitonic effect should appear around 1.1 eV, the oscillator strength of A1 is weak enough and regarded as a forbidden transition. The peak positions of A2–A5 are in almost perfect agreement with the experiment. On the other hand, the oscillator strength of these peaks has a small difference from the experiment; for example, the A3 peak is weaker and the A4 and A5 peaks are stronger than the experiment. By using the GW wave function, the peak heights around 1.8 and 2.5 eV corresponding to A3 and A5 in the dotted line seem slightly closer to each other (see the inset in Fig. 1). This change tends to be close to the experimental spectra. Here, we should mention the difference with the spectra reported in Ref. [8] (not shown in Fig. 1), although a detailed comparison is difficult. One difference from their computational method is that they used the static approximation, which takes a limitation at $\omega = 0$ of the screened Coulomb interaction composing of the direct term $W^d(\omega = 0)$ in a two-particle Hamiltonian. Therefore, the difference between the present result and that in Ref. [8] might be attributed to the dynamical effects. As they pointed out in their paper, the dynamical effects would play a significant role for low-lying exciton.

In the case of Na_6 , the first small peak labeled as B1, which has a very weak oscillator strength, corresponds to the HOMO-LUMO transition. However, the experimental spectra (dashed line) has no corresponding peak. This may be a slight error in our calculation in the oscillator strength, but another possible reason could be because the experiment was performed in the small photon energy range between 1.49 (corresponding to 850 nm) and 3.54 eV (corresponding to 350 nm) [22]. At the higher-energy side, B2 and B3 peak positions agree with the experiment perfectly, and B4 has a little discrepancy by 0.2 eV with the experiment. For Na_8 , we cannot find any significant difference between the present result and the experiment, the small C1 and C2 peaks are again out of the photon energy range in the experiment [23]. The optical absorption spectra of Na_8 have a simple structure. The main peak labeled as C3 in the present result (dotted line) agrees with the experiment

(solid line) almost perfectly. In both cases of Na₆ and Na₈, the use of the GW wave functions (see the inset figures) does not much improve the results using the LDA wave functions. The reason for this is probably because the LUMO level is not very close to the vacuum level in these clusters.

We developed an all-electron first-principles GW + Bethe-Salpeter method with the mixed-basis approach and applied it to the calculation of the optical absorption spectra of Na clusters (Na_{2n}, $n \leq 4$). The resulting spectra, in particular of Na₆ and Na₈, agree with the experiment fairly well. For Na₂ and Na₄, however, the peak positions and the oscillator strengths of some peaks are a little different from the experiment. These discrepancies can be improved at least partly by reconstructing the GW wave functions by taking account of the off-diagonal elements of the GW one-electron self-energy operator minus the LDA exchange-correlation potential, $\langle i | \Sigma^{GW}(\epsilon) - \mu_{xc} | j \rangle$.

Another discrepancy might be caused by the use of the Tamm-Dancoff approximation. In fact, in our previous work on Na₂ in which the full Bethe-Salpeter matrix was treated [9], the agreement with the experiment became slightly better. Recently it was discussed that such an effect becomes larger in shorter polyene chains [16]. So we just state that the effect of the matrix elements of the antiresonant part and the coupling part beyond the Tamm-Dancoff approximation may become larger for smaller clusters. However, the detailed study on this problem is left for future study.

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