First Principles Calculations of Optical Absorption Spectra of Atoms in the Vacuum and Crystals

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Abstract

Starting from the *GW* approximation (GWA) beyond the density functional theory and taking into account the excitonic effect, we have determined optical properties of isolated Zn atom and also Cu impurity atom in NaCl crystal. In the representation of single electron wave functions, we have used the all-electron mixed basis approach in which both plane waves and atomic orbitals are used as a basis set. The resulting quasiparticle energies and optical absorption spectra are compared with available experimental data.

Key words: first principles, quasiparticle energy, optical absorption spectra, many-body perturbation theory, Bethe–Salpeter equation

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1 Introduction

In small clusters, spectra of electronic excited states are strongly dependent on the size of the cluster, and the size control would become a useful technique in the frequency tuning of the excitation spectra of small clusters [1]. In particular, the optical absorption and the fluorescence may play an important role in the application to optical devices, for example.

In spite of these interests, the systematic theoretical study of the spectra of the quasiparticle energies in atomic scale systems in terms of the state-of-the-art *GW* approximation (GWA) [2–4] for the electron self-energy (constructed by the one-particle Green’s function G and the dynamically screened Coulomb interaction W on the basis of the many-body perturbation theory) has been very limited. Moreover, the desirable calculation of the optical absorption spectra of small clusters starting from the GWA and taking the excitonic effect into account for the two-particle Green’s function [5–7] has been very limited also.

Previously some of the present authors have applied the GWA to the calculation of the quasiparticle energy spectra of small clusters such as Li_n , Na_n , K_n [8,9] and Si_n [10]. More recently, Ohno [11] presented a result of optical absorption spectra of alkali-earth atoms and small sodium clusters by starting from the GWA and solving the Bethe–Salpeter (BS) equation for the two-particle Green’s function which takes the excitonic effect into account. The method uses the all-electron mixed basis approach in which one-particle wave functions are expressed by both atomic orbitals and plane waves [7,12–14]. The results are fairly in good agreement with experiments.

In the present report, we will apply this approach to the investigation of the quasiparticle and optical absorption spectra of atoms in the vacuum and crystals. In particular, we treat transition metal elements. This became possible because we have recently made it possible to deal with the d atomic orbitals in our all-electron mixed basis *GW* code. Here, for the system of an isolated atom in the vacuum, we investigate zinc atom, while, for the system of an atomic impurities in crystals, we investigate Cu^+ ion embedded in the sodium-chloride (NaCl) crystal.

For the calculation of Cu^+ ion embedded in the sodium-chloride crystal, we use $2 \times 2 \times 2$ simple cubic supercell and replace one sodium atom with a Cu atom. The position of the Cu atom has been already determined by our previous study using the first-principles structural optimization [15].

The rest of this paper is organized as follows. In section 2, we briefly describe the methodology. In section 3, we present the result of our calculation. We will summarize this paper in section 4.

2 Methodology

Quasiparticle energies of real atomic systems can be calculated accurately by means of the GWA [2–4] which treats the first-order contribution to the self-energy of the one-particle Green’s function G with respect to the dynamically screened Coulomb interaction W given in the random-phase approximation (RPA).

In the GWA, the quasiparticle energies $\varepsilon_n^{\text{QP}}$ and wave functions $\psi_n(\mathbf{r})$ are obtained by solving

$$(T + V_{\text{ext}} + V_H)\psi_n(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_n^{\text{QP}}) \psi_n(\mathbf{r}') = \varepsilon_n^{\text{QP}} \psi_n(\mathbf{r}), \quad (1)$$

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}'; \omega + \omega') W(\mathbf{r}, \mathbf{r}'; \omega') e^{i\eta\omega'}, \quad (2)$$

where T , V_{ext} , V_H , and Σ are the kinetic energy operator, external potential, Hartree potential, and electron self-energy containing the effect of exchange-correlation between electrons, respectively; η is a positive infinitesimal number. W is the dynamically screened Coulomb interaction expressed symbolically as $W = \varepsilon^{-1}U$ in the random phase approximation (RPA), where U is the bare Coulomb interaction and ε is the dielectric function $\varepsilon = 1 - 4\pi P$ (and $P = -iGG$ is the polarizability). Here the generalized plasmon pole model (GPP) [3] is used to evaluate the self-energy. The one-particle Green’s function G is given by

$$G(\mathbf{r}, \mathbf{r}', \omega) = \sum_{n'} \frac{\psi_{n'}(\mathbf{r}) \psi_{n'}^*(\mathbf{r}')}{\omega - \varepsilon_{n'} - i\delta_{n'}}, \quad (3)$$

where $\delta_{n'} = 0^+$ for $\varepsilon_{n'} < \mu_F$ and $\delta_{n'} = 0^-$ for $\varepsilon_{n'} > \mu_F$, provided that μ_F is the Fermi energy. Conventionally $\psi_{n'}(\mathbf{r})$ and $\varepsilon_{n'}^{\text{QP}}$ have been replaced by the LDA wavefunctions and the LDA energy eigenvalues $\varepsilon_{n'}^{\text{LDA}}$. Then, quasiparticle energies are obtained in terms of first-order perturbation theory as

$$\varepsilon_n^{\text{QP}} \approx \varepsilon_n^{\text{LDA}} + \int d\mathbf{r} \int d\mathbf{r}' \psi_n^*(\mathbf{r}) [\Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_n^{\text{QP}}) - \mu_{\text{xc}}^{\text{LDA}}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')] \psi_n(\mathbf{r}'). \quad (4)$$

So far, many calculations with this GWA on the *ab initio* level have been performed for variety of crystals and surfaces [7]. Recently, we have calculated quasiparticle energy spectra of small alkali-metal clusters [8,9] as well as small silicon clusters [10], by using our *GW* code implemented on the all-electron

mixed basis approach [7–11,13,14], in which single particle wave functions are expanded with both plane waves (PW's) and atomic orbitals (AO's).

It has been recognized that spectroscopic properties involving two-particle excitations should be determined still beyond the GWA, i.e., by evaluating accurately the two-particle Green's function. The excitonic effect in the optical absorption spectra can be taken into account by summing the electron-hole ladder diagrams, which become important in particular at short distances, in the two-particle Green's function. This can be formulated by using the functional derivative of the electron self-energy $U^{\text{Hartree}} + \Sigma^{GW}$ with respect to the one-particle Green's function G . Thus derived equation is the BS equation for the two-particle Green's function, $S(1, 1'; 2, 2') = S(\mathbf{r}_1, t_1, \mathbf{r}'_1, t'_1; \mathbf{r}_2, t_2, \mathbf{r}'_2, t'_2)$, [7]

$$S(1, 1'; 2, 2') = S_0(1, 1'; 2, 2') + S_0(1, 1'; 3, 3')\Xi(3, 3'; 4, 4')S(4, 4'; 2, 2'). \quad (5)$$

Here, $S_0(1, 1'; 2, 2') = G(1', 2')G(2, 1)$ is the unperturbed function, in which the disconnected term $-G(1, 1')G(2, 2')$ is excluded. (The notation $G(1, 2) = G(\mathbf{r}_1, \mathbf{r}_2; t_1 - t_2)$ is used to express the one-particle Green's function.) The interaction kernel Ξ , which stands for the irreducible electron-hole interaction, is determined by $\Xi = \delta(U^{\text{Hartree}} + \Sigma^{GW})/\delta G$ and contains two different contributions

$$\Xi(1, 1'; 2, 2') = -i\delta(1, 1')\delta(2, 2')U(1, 2) + i\delta(1, 2)\delta(1', 2')W'(1, 1'), \quad (6)$$

where $U(1, 2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ comes from the functional derivative of the Hartree term (U^{Hartree}), and $-W'(1, 1')$ represents the screened Coulomb attraction coming from the functional derivative of the GW self-energy (Σ^{GW}).

To solve (6), one has to invert a four-point function $I - S_0\Xi$, where I is the identity operator. Strinati [16] derived a simplified eigenvalue equation which can be used to bypass the matrix inversion of the BS equation. Strinati treated positive frequency part only. Albrecht *et al.* [5] derived and applied a similar eigenvalue equation with static approximation (they treated negative frequency part as well). Rohlfing and Louie [6] applied the Strinati scheme combined with the generalized plasmon-pole model. All these authors have replaced the kernel W' with the dynamically screened interaction W , which is equivalent to neglecting the term $G\delta W/\delta G$ in $\delta\Sigma/\delta G$ [16]. For the contribution of this $G\delta W/\delta G$ as well as the negative frequency part, an analysis is given by Ohno [11].

The basic equation stands for [17]

$$(\varepsilon_c^{\text{QP}} - \varepsilon_v^{\text{QP}})A_{vc} + \sum_{v'c'} \{2X_{vc;v'c'}\delta_{M,0} - W_{vc;v'c'}(\Omega)\}A_{v'c'} = \Omega A_{vc}. \quad (7)$$

In (7), the exchange term X exists only for singlet exciton, having spin multiplicity $M = 0$. Moreover, if only one diagonal element between $v = v' = \text{HOMO}$ and $c = c' = \text{LUMO}$ dominates the others, the magnitude of the singlet-triplet splitting in the optical absorption peaks amounts to $2X_{vc;vc}$, which is a well known result.

In the following calculation of Zn, a rhombohedral fcc supercell is used with a cubic edge of 30 a.u.. As a basis functions, 2975 PW's corresponding 8.7 Ry cutoff energy as well as $1s$, $2s$, $2p$, $3s$, $3p$, $3d$ and $4s$ AO's are used. In the evaluation of matrix elements, 2975 $\mathbf{G}(\mathbf{G}')$ vectors corresponding 8.7 Ry cutoff energy are used for $\Sigma_c(\omega)$ and $(W - U)$, and 40857 $\mathbf{G}$ vectors corresponding 50 Ry cutoff energy are used for Σ_x and U . In addition, integrations along the radial coordinate are used to evaluate matrix elements of Σ_x and U sandwiched by the on-site AO's only. In the calculation of Cu impurity in sodium-chloride crystal, $2 \times 2 \times 2$ simple-cubic unit cell is employed, and only Γ point is used in place of doing the k -point sampling. According to our separate study on the optimal position of the Cu atom [15], we assume two possibilities for the position of the Cu atom: One is the on-center position and the other is the off-center position 7% deviated along the (111) axis, i.e. (0.57,0.57,0.57). The local relaxation of the ligand crystal is also taken into account in the present calculation.

3 Results

First we present the result of Zn atom. Table 1 lists all the terms contributing the GW quasiparticle energies of the HOMO ($4s$) state and the LUMO ($4p$) states. The columns indicated as 'exact' represent the values computed directly with the Herman-Skillman atomic code, which can give exact LDA values for isolated atoms. The experimental value for the HOMO state is the ionization potential with a minus sign. An excellent agreement is achieved between the resulting GW quasiparticle energy and the experimental value. The resulting optical absorption peak energy of isolated Zn atom is presented in Table 2 together with the experimental value. The energy depends on the character of the excited states, either the singlet ($^1S \rightarrow ^1P$) exciton or the triplet ($^1S \rightarrow ^3P$) exciton. Agreement between the present result and the experimental value is fairly good, but the singlet-triplet (exchange) splitting is slightly larger than the experimental value. This is a common feature of the present method [11,17] and due to the fact that the amount of this exchange splitting is directly related to the exchange integral sandwiched by the LDA wave functions. Only the absolute values of singlet and triplet absorption energies reflect the details of the Bethe-Salpeter equation and their difference (i.e., the exchange splitting) does not directly.

Table 1

Contributions to the quasiparticle energies (in eV) for the HOMO and LUMO states are shown for Zn atom compared with the experimental ionization potential and negative of the electron affinity ($-E^{\text{EXP}}$). $\mu_{xc,n}^{\text{LDA}} = \langle n | \mu_{xc}^{\text{LDA}} | n \rangle$ means the expectation value of the LDA exchange-correlation potential, $\Sigma_{x,n}$ and $\Sigma_{c,n}$ are, respectively, the Fock exchange part and the correlation part of the self-energy Σ .

	ϵ_n^{LDA}	$\mu_{xc,n}^{\text{LDA}}$	$\Sigma_{x,n}$	$\Sigma_{c,n}$	E^{GWA}	E^{EXP}
4s	-6.07	-9.91	-12.11	-1.40	-9.41	-9.39
'exact'	-6.06	-9.93	-12.36			
4p	-1.32	-5.39	-2.38	-0.62	+0.96	(0.00)
'exact'	-1.28	-5.56	-2.51			

Table 2

The optical absorption peak energy (in eV) of Zn atom corresponding to the singlet or triplet transition calculated from the BS equation. The experimental value is also listed for comparison.

Transition	Present result	Experiment
singlet	6.17	5.78
triplet	3.84	4.01

Table 3

Energy gap estimated with the LDA (E_g^{LDA}) or with the GWA (E_g^{GWA}) for the pure sodium-chloride crystal and the system with Cu impurity. The experimental value (E_g^{EXP}) is shown for the pure crystal.

	E_g^{LDA}	E_g^{GWA}	E_g^{EXP}
NaCl	4.82	9.02	8.5
NaCl:Cu	2.98	8.00	

Next we turn our attention to the sodium-chloride crystal. In Table 2, the band gap estimated from the quasiparticle energies of the top of the valence band and the bottom of the conduction band calculated within the LDA or within the GWA is shown for the pure sodium-chloride crystal and the system with Cu impurity. The experimental value for the pure crystal is also shown for comparison in this table.

In Fig. 1, the resulting optical absorption spectra of the Cu impurity system are superposed with those of the pure alkali-chloride crystal, in order to sim-

ulate the situation of the dilute impurity concentration. The first absorption peak of Cu^+ ion is located slightly lower in photon energy than that of the pure sodium-chloride crystal. Two (solid and dashed) curves correspond, respectively, the cases of the on-center position and the off-center position of the Cu atom. Its peak position does not depend on the location of the Cu ion but its peak height depends. This is due to the transition from $3d^{10}$ to $3d^9 4s^1$ is the dipole forbidden in the case of the isolated Cu^+ ion. When the Cu ion is put in the ligand field, the spherical symmetry is broken and the transition becomes partially allowed. The more deviated the location of the Cu ion from the on-center position, the stronger this tendency. These resulting characteristics of the absorption spectra are also consistent with the experiment done by Nagasaka [18,19].

Fig. 1. The calculated photo-absorption spectra of the NaCl:Cu system.

4 Concluding Remarks

In the paper, we have presented our result of quasiparticle energies and optical absorption spectra of an isolated zinc atom and Cu^+ ions in sodium-chloride crystal. The quasiparticle energies are calculated by the GWA, and the optical absorption spectra are calculated by starting from the GWA and solving the BS equation to take into account the excitonic effect. In the former case, the agreement between our result and the experiment is fairly good, which means the potential ability of the present method. In the latter case, our

result is consistent with the experiment, i.e., the tendency of the spectrum depending on the position of the Cu atom is similar to that expected in the experiment. although only Γ -point calculation is used instead of the k -point sampling. In contrast to the conventional quantum chemistry approach such as the configuration interaction (CI) or the multi-reference CI, the present method has an advantage that it can reproduce the spectra of one-particle (quasiparticle) energies and electron-hole (optical absorption) energies all at once without assuming any symmetry of the excited states. The symmetry of the excited states can be seen from the character of the resulting eigenvectors, if needed. The disadvantage of the present method is the computational time which scales as N^6 when the number of electrons N increases, although the CI calculation is known to scale roughly as N^7 .

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