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Computational Materials Science 36 (2006) 125–129

COMPUTATIONAL MATERIALS SCIENCE

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First-principles calculations of optical absorption spectra of atoms in the vacuum and crystals

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Received 14 July 2004; accepted 13 January 2005

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 quasipartile energies and optical absorption spectra are compared with available experimental data.

Keywords: First-principles; Quasiparticle energy; Optical absorption spectra; Many-body perturbation theory; Bethe–Salpeter equation

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

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doi:10.1016/j.commatsci.2005.01.017

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 $2\times2\times2$ 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 $\varepsilon_n^{\rm QP}$ and wave functions $\psi_n(\boldsymbol{r})$ are obtained by solving

$$(T + V_{\rm ext} + V_{\rm H})\psi_n(\boldsymbol{r}) + \int {\rm d}\boldsymbol{r}'\Sigma(\boldsymbol{r},\boldsymbol{r}';\varepsilon_n^{\rm QP})\psi_n(\boldsymbol{r}') = \varepsilon_n^{\rm QP}\psi_n(\boldsymbol{r}), \tag{1}$$

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

where T, $V_{\rm ext}$, $V_{\rm H}$, 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 $P = -{\rm i}GG$ 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

$$G(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{n'}\frac{\psi_{n'}(\boldsymbol{r})\psi^*_{n'}(\boldsymbol{r}')}{\omega-\varepsilon_{n'}-i\delta_{n'}}, \tag{3}$$

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 Conventionally $\psi_{n'}(\boldsymbol{r})$ and $\varepsilon_{n'}^{\rm QP}$ have been replaced by the LDA wave-functions and the LDA energy eigenvalues $\varepsilon_{n'}^{\rm LDA}$.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

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

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 $U^{\rm Hartree} + \Sigma^{\rm GW}$ with respect to the one-particle Green's function G. Thus derived equation is the BS equation for the two-particle Green's function, $S(1,1';2,2') = S(\boldsymbol{r}_1,t_1,\boldsymbol{r}_1',t_1';\boldsymbol{r}_2,t_2,\boldsymbol{r}_2',t_2')$, [7]

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

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 $G(1,2) = G(\boldsymbol{r}_1,\boldsymbol{r}_2;\ t_1-t_2)$ 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 $\Xi = \delta(U^{\rm Hartree} + \Sigma^{\rm GW})/\delta G$ and contains two different contributions

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

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

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.