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Ab Initio All-Electron *GW* Calculation of Lithium Chloride Crystal

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In order to determine the band gap and quasiparticle energies of lithium chloride crystal accurately, we employ the state-of-the-art *GW* approximation on the basis of many-body-perturbation-theory at the *ab initio* level. Our method is based on the all-electron mixed-basis approach. We use the $2 \times 2 \times 2$ supercell in which four lithium and four chlorine atoms exist. We demonstrate the importance of the **q** point sampling for the momentum transfer **q** of the Coulomb matrix elements. The result for the direct band gap at the Γ point compares well with experiment and the previous calculations.

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1. Introduction

Recently the first principles methods on the basis of the density functional theory (DFT)[1] and the local density approximation (LDA)[2] have been extensively used in the solid state physics. They are capable to predict correctly the ground state properties of variety of materials. In spite of this great success, the LDA fails to predict correctly the energy band gap of insulators. It underestimates typically $30 \sim 50\%$ of the experimental band gap which is obtained by the photoemission spectroscopy.

In order to detemine correctly the band gap of insulators, it is necessary to go beyond the framework of the DFT. In the case of alkali chloride (or fluoride) crystals, Erwin and Lin[3] attempted to include the self-interaction correction in the band structure calculation. They determined the band gap of lithium chloride to be 10.0 eV. A more sophisticated modern approach is the so-called *GW* approximation (GWA), which is based on the many-body-perturbation-theory at the *ab initio* level.[4–7] So far, there have been many efforts in the application of the GWA, for example, to the semiconductors, surfaces and clusters.[8] Among them, Hybertsen and Louie[5] and Shirley[9] determined the band gap of lithium chloride crystal to be 9.1 eV and 9.2 eV, which are in good agreement with the experimental value of 9.4 eV.[10] Their method is based on the pseudopotential approach.

The aim of the present calculation is to adapt an *ab initio* all-electron GWA calculation to the crystal system. We will determine the band gap and quasiparticle energies of lithium chloride and compare the result with the previous calculations using the pseudopotential approach. Our all-electron *GW* code is based on the all-electron mixed-basis approach. In this approach, each one-particle wave function is expressed in a linear combination of plane waves (PWs) and atomic orbitals (AOs). The AOs are generated by a modified Herman-Skilman's code[11] which uses logarithmic mesh in radial direction and by smoothly cutting the tail within the non-overlapping atomic sphere. This approach can describe well both the spatially extended states and the localized states with relatively small number or basis functions.[12–15] So far, we applied successfully this all-electron *GW* code to the calculation of several alkali-metal clusters[16,17] and small silicon clusters.[18] In the present work, we newly implement the **q** point sampling in our all-electron *GW* code as will be described below in detail. Then we perform a supercell GWA calculation for lithium chloride crystal.

2. Methodology

Our formulation of the *ab initio* all-electron GWA is essentially based on the original paper by Hybertsen and Louie[4,5] who used the pseudopotential approach. We start from the calculation at the LDA level, and determine the state functions $|n\mathbf{k}\rangle$ and the energy eigenvalues $\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}}$. In the GWA, the quasiparticle energies $E_{n\mathbf{k}}$ can be obtained by solving the Dyson equation,

$$(T + V_{\mathrm{nuc}} + V_{\mathrm{H}})|n\mathbf{k}\rangle + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_{n\mathbf{k}})|n\mathbf{k}\rangle = E_{n\mathbf{k}}|n\mathbf{k}\rangle, \tag{1}$$

perturbatively to the first order. Here, T, V_{nuc}, V_{H}, and Σ are the kinetic energy operator, the nucleus Coulomb potential, Hartree potential and the self-energy operator. In the GWA, the self-energy operator is approximated in a form

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

where G is the one-particle Green's function in the LDA and W is the dynamically screend Coulomb interaction within the random phase approximation (RPA),[19,20] and η is a positive infinitesimal number. The dynamically screened interaction in Fourier space is related to the dielectric matrix by

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = [\varepsilon^{-1}]_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) v(\mathbf{q} + \mathbf{G}'), \tag{3}$$

where $v(\mathbf{q} + \mathbf{G}) = 4\pi/\Omega|\mathbf{q} + \mathbf{G}|^2$ is the Coulomb potential in Fourier space (Ω is the volume of the unit cell), and $\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)$ is the dielectric matrix defined by

$$\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) = \delta_{\mathbf{G}\mathbf{G}'} - v(\mathbf{q} + \mathbf{G}) P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega), \tag{4}$$

with the polarizability function in the RPA,

$$P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega = 0) = \sum_{nn_1\mathbf{k}} \langle n\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n_1\mathbf{k} + \mathbf{q}\rangle \langle n_1\mathbf{k} + \mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\mathbf{k}\rangle$$

$$\times \frac{f(\varepsilon^{\mathrm{LDA}}_{n_1\mathbf{k}+\mathbf{q}}) - f(\varepsilon^{\mathrm{LDA}}_{n\mathbf{k}})}{\varepsilon^{\mathrm{LDA}}_{n_1\mathbf{k}+\mathbf{q}} - \varepsilon^{\mathrm{LDA}}_{n\mathbf{k}}}, \tag{5}$$

where $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors, and $f(\varepsilon)$ denotes the Fermi-Dirac distribution function. The matrix elemtents in the numerator involve the intermediate states $|n_1\mathbf{k}+\mathbf{q}\rangle$. Since we use a large supercell, we treat only the Γ point ($\mathbf{k}=0$) contribution. But we evaluate this polarizability function for many different $\mathbf{q}$ points. This is because there is a singularity in the small momentum transfer limit ($\mathbf{q}\to 0$) of the Coulomb interaction appearing in the matrix elements of the self-energy operator.

The self-energy operator Σ can be divided into two parts: one is the Fock exchange part $\Sigma_{\mathrm{x}}(\mathbf{r},\mathbf{r}')$ and the other is the correlation part $\Sigma_{\mathrm{c}}(\mathbf{r},\mathbf{r}';E)$. The expectation values of the Fock exchange contribution are given by

$$\begin{aligned}\Sigma_{x,n\mathbf{k}} &= \langle n\mathbf{k}|\Sigma_{\mathrm{x}}(\mathbf{r},\mathbf{r}')|n\mathbf{k}\rangle \\ &= \sum_{n_1}^{occ}\sum_{\mathbf{qG}}\langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n_1\mathbf{k}-\mathbf{q}\rangle \\ &\quad\times\langle n_1\mathbf{k}-\mathbf{q}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}|n\mathbf{k}\rangle v(\mathbf{q}+\mathbf{G}),\end{aligned} \tag{6}$$

while for the correlation part of the self-energy, the generalized plasmon-pole model[5] is used to bypass the calculation of the ω dependence of the dielectric matrices and the ω'-integration in eq. (2). Then the expectation values of the correlation part are given by

$$\begin{aligned}\Sigma_{c,n\mathbf{k}}(E) &= \langle n\mathbf{k}|\Sigma_{\mathrm{c}}(\mathbf{r},\mathbf{r}';E)|n\mathbf{k}\rangle \\ &= \sum_{n_1}^{occ}\sum_{\mathbf{qGG}'}\langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n_1\mathbf{k}-\mathbf{q}\rangle \\ &\quad\times\langle n_1\mathbf{k}-\mathbf{q}|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\mathbf{k}\rangle \\ &\quad\times\frac{1}{2}\frac{\Omega^2_{\mathbf{GG}'}(\mathbf{q})}{\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})[E-\varepsilon^{\mathrm{LDA}}_{n_1\mathbf{k}-\mathbf{q}}+\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})]}v(\mathbf{q}+\mathbf{G}') \\ &\quad+\sum_{n_1}^{emp}\sum_{\mathbf{qGG}'}\langle n\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n_1\mathbf{k}-\mathbf{q}\rangle \\ &\quad\times\langle n_1\mathbf{k}-\mathbf{q}|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n\mathbf{k}\rangle \\ &\quad\times\frac{1}{2}\frac{\Omega^2_{\mathbf{GG}'}(\mathbf{q})}{\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})[E-\varepsilon^{\mathrm{LDA}}_{n_1\mathbf{k}-\mathbf{q}}-\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})]}v(\mathbf{q}+\mathbf{G}'),\end{aligned} \tag{7}$$

where $\tilde{\omega}_{\mathbf{GG}'}$ and $\Omega^2_{\mathbf{GG}'}(\mathbf{q})$ are the same functions as those defined in the paper by Hybertsen and Louie.[5] The summations with respect to n_1 in eqs. (6) and (7) run occupied or empty states only, according to the symbol *occ* or *emp*. The matrix elemtents in the numerator involve the intermediate states $|n_1\mathbf{k}-\mathbf{q}\rangle$. For $\mathbf{k}=0$, these states can be constructed by imposing the inversion operation onto the states $|n_1\mathbf{k}+\mathbf{q}\rangle$ which are needed in the evaluation of the polarizability [see eq. (5)]. Here we assume just $\mathbf{k}=0$ in our supercell calculation, but the *X* point can be discussed as well as the Γ point because of the folding of the first Brillouin zone. On the other hand, we perform $\mathbf{q}$ point sampling explicitly in evaluating eqs. (6) and (7).

Finally the quasiparticle energies are obtained in terms of the first-order perturbation theory as

$$\begin{aligned}E^{\mathrm{GWA}}_{n\mathbf{k}} &\approx \varepsilon^{\mathrm{LDA}}_{n\mathbf{k}} + \frac{1}{1-(\partial\Sigma(\omega)/\partial\omega)_{\varepsilon^{\mathrm{LDA}}_{n\mathbf{k}}}} \\ &\quad\times\langle n\mathbf{k}|\Sigma(\varepsilon^{\mathrm{LDA}}_{n\mathbf{k}}) - \mu^{\mathrm{LDA}}_{xc}|n\mathbf{k}\rangle,\end{aligned} \tag{8}$$

where the denomenator in the second term is necessary to use the LDA eignvalues $\varepsilon^{\mathrm{LDA}}_{n\mathbf{k}}$ as the argument of the self-energy operator in the numerator.

3. Results

In the present calculation, we assume the $2\times2\times2$ simple cubic supercell of the LiCl crystal with the edge length of 0.514 nm, and use 24 numerical AOs and 1419 PWs corresponding to 279 eV (20.5 Ry) cutoff energy. For the evaluation of $P_{\mathbf{GG}'}(\mathbf{q},\omega=0)$ and $\Sigma_{\mathrm{c},n\mathbf{k}}$, 500 states are used in the summation over n_1 in eqs. (5) and (7), and 2109 $\mathbf{G}(\mathbf{G}')$ corresponding to 354 eV (26 Ry) cutoff energy are used. On the other hand, in the calculation of $\Sigma_{\mathrm{x},n\mathbf{k}}$, 24405 $\mathbf{G}$ corresponding to 1845 eV (136 Ry) cutoff energy are used to take into account correctly the core contribution.

We have first compaired the Γ point only calculation and the calculation using 4 special points at the LDA level, and confirmed that there is only negligible difference between their results (only 0.01 eV difference in the LDA gap). Therefore we perform Γ point only calculation also at the GWA level. On the other hand, for the calculation of $\varepsilon_{\mathbf{GG}'}(\mathbf{q},0)$, $\Sigma_{\mathrm{x},n\mathbf{k}}$ and $\Sigma_{\mathrm{c},n\mathbf{k}}(\varepsilon^{\mathrm{LDA}}_{n\mathbf{k}})$, we use 20 $\mathbf{q}$ points in the irreducible wedge of the Brillouine zone. Table 1 shows the

Table 1 The $\mathbf{q}$ dependence of the (exchange) contributions to $\Sigma_{\mathrm{x},n\mathbf{k}}$ and the (correlation) contributions to $\Sigma_{\mathrm{c},n\mathbf{k}}(\varepsilon^{\mathrm{LDA}}_{n\mathbf{k}})$ in eqs. (6) and (7) at the top of the valence band (Γ_{15v}) and at the bottom of the conduction band (Γ_{1c}). The values are given in units of eV. The notation $(l,m,n)/8$ indicates the $\mathbf{q}$ point, $(\pi/a)(l/8,m/8,n/8)$, inside the 1/48 irreducible wedge of the simple-cubic first Brillouine zone.

	contribution to $\Sigma_{\mathrm{x},n\mathbf{k}}$		contribution to $\Sigma_{\mathrm{c},n\mathbf{k}}(\varepsilon^{\mathrm{LDA}}_{n\mathbf{k}})$	
	Γ_{15v}	Γ_{1c}	Γ_{15v}	Γ_{1c}
(1,1,1)/8	−82.41	7.91	−0.39	−1.72
(3,3,3)/8	−21.63	−6.78	−0.42	−1.81
(3,1,1)/8	−32.67	−4.35	−0.40	−1.77
(3,3,1)/8	−24.82	−6.13	−0.40	−1.80
(5,5,5)/8	−16.54	−7.68	−0.49	−1.82
(7,7,7)/8	−14.64	−7.96	−0.60	−1.63
(7,5,5)/8	−15.71	−7.80	−0.52	−1.79
(7,7,5)/8	−15.10	−7.89	−0.56	−1.72
(5,1,1)/8	−21.58	−6.87	−0.42	−1.87
(7,1,1)/8	−18.06	−7.49	−0.40	−2.02
(5,3,3)/8	−18.72	−7.35	−0.44	−1.85
(7,3,3)/8	−16.93	−7.65	−0.46	−1.93
(5,3,1)/8	−19.82	−7.18	−0.42	−1.86
(7,3,1)/8	−17.41	−7.58	−0.43	−1.98
(5,5,1)/8	−17.90	−7.51	−0.44	−1.87
(5,5,3)/8	−17.35	−7.57	−0.45	−1.84
(7,7,1)/8	−15.60	−7.83	−0.55	−1.86
(7,7,3)/8	−15.43	−7.85	−0.55	−1.81
(7,5,1)/8	−16.49	−7.71	−0.48	−1.91
(7,5,3)/8	−16.20	−7.74	−0.49	−1.86

Table 2 The LDA eigenvalues $\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}}$ and the GWA quasiparticle energies $E_{n\mathbf{k}}^{\mathrm{GWA}}$ estimated at the levels in the vicinity of the band gap of lithium chloride crystal (in units of eV). Contributions to the quasiparticle energies are also shown: $\mu_{\mathrm{xc},n\mathbf{k}}^{\mathrm{LDA}} = \langle n\mathbf{k}|\mu_{\mathrm{xc}}^{\mathrm{LDA}}|n\mathbf{k}\rangle$, $\Sigma_{\mathrm{x},n\mathbf{k}} = \langle n\mathbf{k}|\Sigma_{\mathrm{x}}|n\mathbf{k}\rangle$, and $\Sigma_{\mathrm{c},n\mathbf{k}}(\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}}) = \langle n\mathbf{k}|\Sigma_{\mathrm{c}}(\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}})|n\mathbf{k}\rangle$ are the expectation values of, respectively, the LDA exchange-correlation potential, the exchange part [eq. (6)] and the correlation part [eq. (7)] of the self-energy operator Σ. There is no special meaning in the energy zero of $\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}}$ and $E_{n\mathbf{k}}^{\mathrm{GWA}}$, *i.e.*, these values may contain arbitrary shift by a constant value.

	$\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}}$	$\mu_{\mathrm{xc},n\mathbf{k}}^{\mathrm{LDA}}$	$\Sigma_{\mathrm{x},n\mathbf{k}}$	$\Sigma_{\mathrm{c},n}(\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}})$	$E_{n\mathbf{k}}^{\mathrm{GWA}}$
Γ_{1c}	7.98	−11.31	−7.10	−1.86	10.07
Γ_{15v}	1.84	−17.06	−19.44	−0.46	−0.17
X'_{5v}	0.70	−15.68	−18.14	−0.45	−1.98
X'_{4v}	−1.16	−13.71	−16.33	−0.49	−3.99

q dependence of the (exchange) contributions to $\Sigma_{\mathrm{x},n\mathbf{k}}$ and the (correlation) contributions to $\Sigma_{\mathrm{c},n\mathbf{k}}(\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}})$ in eqs. (6) and (7) (the expectation values of the self-energy operator) at the valence band top (Γ_{15v}) and the conduction band bottom (Γ_{1c}). There is a large exchange contribution in the vicinity of the Γ point, (0,0,0), although no such large contribution appears in the correlation term (see, for example, the discussion given in Appendix B in Ref. 5). We have confirmed that 20 **q** points are required in the **q** point sampling.

Table 2 lists the separate contributions to the *GW* quasiparticle energies for several valence and conduction levels at the Γ and X points of lithium chloride, as well as the final result $E_{n\mathbf{k}}^{\mathrm{GWA}}$ calculated with eq. (8). The listed contributions, $\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}}$, $\mu_{\mathrm{xc},n\mathbf{k}}^{\mathrm{LDA}}$, $\Sigma_{\mathrm{x},n\mathbf{k}}$, and $\Sigma_{\mathrm{c},n\mathbf{k}}(\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}})$ represent the expectation values of, respectively, the LDA (Kohn-Sham) Hamiltonian, the LDA exchange-correlation potential, and the exchange (Σ_{x}) and correlation (Σ_{c}) parts of the self-energy. There is no meaning in the energy zero of $E_{n\mathbf{k}}^{\mathrm{GWA}}$ as well as $\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}}$ because the energy zero is not determined correctly by the standard crystal calculation at the LDA level. The level symbols, Γ_{15v} and Γ_{1c}, denote the top of the valence band and the bottom of the conduction band, respectively. The estimated band gap between these two levels is 10.2 eV. This value is slightly larger than but not much different from the experimental value of 9.4 eV, and the previous *GW* calculations[5,9] using the pseudopotential approach (9.1-2 eV).

4. Concluding Remarks

In this paper, we have newly implemented the **q** point sampling in the all-electron mixed-basis *GW* code and applied it to LiCl crystal. We have investigated the **q** dependence of the exchange and correlation contributions to the self-energy, and demonstrated explicitly that the importance of the **q** point sampling. We have presented the quasiparticle energies at several levels close to the band gap. The resulting direct band gap between Γ_{15v} and Γ_{1c} is compared successfully with the experimental value and the values given in the previous calculations based on the GWA pseudopotential approach. This indicates that the present approach works well for insulators such as LiCl. We are now planning to extend the present calculation to a different kind of insulators.

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