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# Dielectric Response Functions Studied by an All-Electron Mixed-Basis Approach

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Dielectric response functions for Si and GaAs, which include local-field effects and frequency dependence, are calculated within the Local Density Approximation (LDA) using our original all-electron mixed-basis approach program. The results are in good agreement with other calculations. The local-field effects are small but not negligible for these materials.

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## I. Introduction

Dielectric properties of materials have a fundamental importance<sup>(1)</sup>. They are characterized by the dielectric response function which represents screening effects of Coulomb interactions between electrons, and are related to optical properties of materials. If nearly homogeneous systems are considered, one needs not to discuss the nonlocality of short-range interactions between electrons because of the full translational symmetry. If we discuss inhomogeneous systems such as semiconductors whose electrons are comparatively localized, the effects of short-range interactions and thus local-field effects become important. Calculations of frequency-dependent dielectric functions including local-field effects have already been done by Louie *et al.*<sup>(2)</sup> and Hybertsen *et al.* for Si<sup>(3)(4)</sup> by an empirical pseudopotential method within the local density approximation (LDA). We have extended their research by calculating the dielectric response functions for Si and GaAs by an *ab initio* all-electron mixed-basis approach.

Since the calculation of a dielectric response function within the random phase approximation (RPA)<sup>(5)</sup> is very time consuming by first-principles, only few results have been published<sup>(2)-(4)</sup>. This quantity is important not only because it is a fundamental property of materials but also because it is required for the *GW* approximation<sup>(6)</sup>. In the present paper, we will present the theoretical results of the dielectric response function of Si and GaAs by using our original all-electron mixed-basis approach program. The rest of this paper is organized as follows: In Section 2, the methodology is described shortly. The results and discussions are presented in Section 3. Lastly, Section 4 is devoted to the conclusion.

## II. Methodology

Within the random phase approximation (RPA)<sup>(5)</sup> the dielectric response function  $\epsilon_{G,G'}(\mathbf{q}, \omega)$  is given by

$$\epsilon_{G,G'}(\mathbf{q}, \omega) = \delta_{G,G'} - v(\mathbf{q} + \mathbf{G})P_{G,G'}(\mathbf{q}, \omega), \quad (1)$$

with the Coulomb potential

$$v(\mathbf{q}) = \frac{4\pi e^2}{\Omega |\mathbf{q}|^2} \quad (2)$$

and the polarizability function

$$P_{G,G'}(\mathbf{q}, \omega) = \sum_{\mathbf{k}} \sum_{n,n'} \langle \mathbf{k}, n | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | n', \mathbf{k} + \mathbf{q} \rangle \times \langle \mathbf{k} + \mathbf{q}, n' | e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | n, \mathbf{k} \rangle \times \frac{f_0(E_{n',\mathbf{k}+\mathbf{q}}) - f_0(E_{n,\mathbf{k}})}{E_{n',\mathbf{k}+\mathbf{q}} - E_{n,\mathbf{k}} - \omega - i\delta}, \quad (3)$$

where  $\Omega$  is the volume of unit cell.

The summation of wave vector  $\mathbf{k}$  runs over all special points inside the first Brillouin Zone (BZ), or inside the irreducible BZ (IBZ). If the summation runs just inside IBZ, then we must operate symmetry operations of crystals unless both  $\mathbf{G}$  and  $\mathbf{G}'$  are zero.  $E_{n,\mathbf{k}}$  and  $E_{n',\mathbf{k}+\mathbf{q}}$  are energy eigenvalues of level  $n$  and  $n'$  at  $\mathbf{k}$  and  $\mathbf{k} + \mathbf{q}$ , respectively.  $\mathbf{G}$  and  $\mathbf{G}'$  are reciprocal lattice vectors, representing local-field effects.  $\omega$  and  $f_0(E)$  denote frequency and Fermi-Dirac distribution function, respectively. The physical meaning of this equation, roughly speaking, is the response of the  $\mathbf{G}$  component of an induced charge to the  $\mathbf{G}'$  component of a test charge. The photon wave vector  $\mathbf{q}$  is so small that we can discuss only the limit  $\mathbf{q} \rightarrow 0$ . That is, we may only consider the case where an electron transition from an occupied band to a higher conduction band occurs vertically. In homogeneous systems one may consider only the case  $\mathbf{G} = \mathbf{G}' = (0, 0, 0)$ , but in inhomogeneous systems such as semiconductors we need nonzero  $\mathbf{G}$  and  $\mathbf{G}'$ . We have performed this calculation based on a first-principle, all-electron calculation mixed-basis approach<sup>(7)</sup>. The mixed basis approach was originally introduced by Louie, Ho and Cohen<sup>(8)</sup> in order to treat localized  $3d$  orbitals within the pseudopotential formalism. The present all-electron mixed-basis approach is a natural extension of the pseudopotential approach to take into account fully the core electrons. Here, the crystalline core wavefunctions are

mainly expressed by the core orbitals of isolated atoms. The crystalline valence wavefunctions are expanded using the atomic core orbitals (AO) and plane waves. The atomic wavefunctions are evaluated on a radial logarithmic mesh, which allows an accurate description in the vicinity of nuclei. We replace the potential experienced by the core atomic orbitals with spherically averaged value, since the core region is usually very small and the potential is mostly spherically symmetric around the nuclei. Then all the matrix elements are accurately evaluated by using a fast Fourier transformation or one-dimensional spline integral along the radial (logarithmic) mesh. The present all-electron mixed-basis approach has successfully been applied to *ab initio* calculations of the magnetic susceptibility<sup>(9)</sup> and also to *ab initio* molecular dynamics<sup>(10)(11)</sup>.

### III. Results and Discussion

We have used Perdew and Zunger's exchange-correlation potential<sup>(12)</sup> and Herman and Skillman numerical basis for AO<sup>(13)</sup>. The cut-off energy is 48 and 44 Ry for Si and GaAs, respectively. Lattice constants are  $5.43 \times 10$  nm and  $5.65 \times 10$  nm for Si and GaAs, respectively, which are taken from experiments. We have divided the unit cell into  $32 \times 32 \times 32$  grids in real space (global space). For all the cases total number of iterations of Hamiltonian diagonalization are 50 times, and charge mixing rate is 90%. We have calculated with the special  $k$ -points method for all materials. We have used 408  $k$ -points in the IBZ for these materials. If we calculate only static dielectric constants, we need only about 10  $k$ -points. However, to estimate the frequency dependence of dielectric constants at least 400  $k$ -points are needed. Screening effect increases with  $\epsilon(q, \omega)$  through eq. (1).

**Figure 1(a)** shows frequency dependence of the dielectric response function for  $G=G'=q=(0, 0, 0)$  in eq. (2). At  $\omega=0$ , the value for our calculated static dielectric constant is 14.5, which is a little larger than the experimental value of 12.0. It is well known that LDA underestimates the band gap of semiconductors and insulators, hence the energy denominator between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) in eq. (3) is less than the corresponding experimental value. The real part of dielectric constant is, therefore, a little greater than the experimental value. As the frequency increases from zero, the real part of  $\epsilon$  is increasing up to about 34 at 2.5 eV which is the LDA band gap at  $\Gamma$ -point, and then decreasing to negative value at about 4 eV. And then increasing up to zero with the frequency ( $\omega < 15$  eV). The imaginary part,  $\epsilon_2$ , is larger than zero at any frequency. The main peak of the imaginary part occurs at about 4 eV, since the gap between HOMO and LUMO levels is about 4 eV at most of the energy points in the Brillouin Zone. Similar calculations have been done for Si by using pseudopotentials by Louie *et al.*<sup>(2)</sup> and Hybertsen *et al.*<sup>(3)</sup>. Our results are in good agreement with their calculations.

**Figure 1(b)** shows frequency dependence of the die-

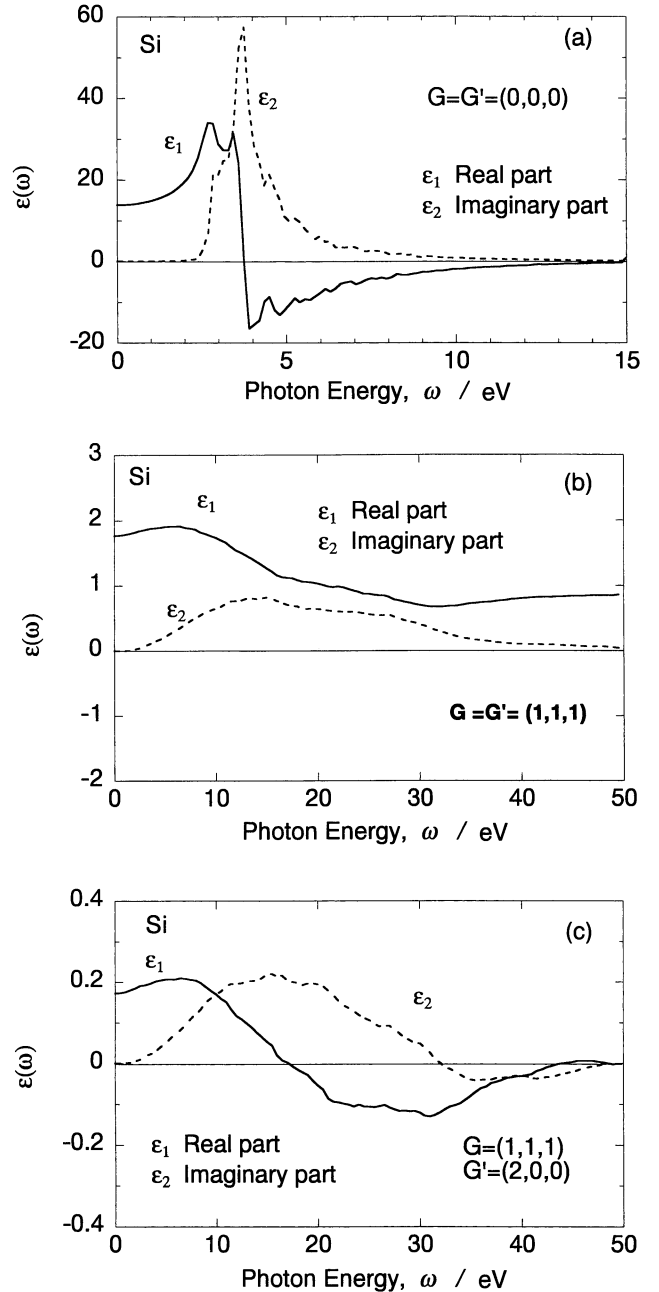


Fig. 1 Real and imaginary parts of the presently calculated elements of the dielectric matrix based on the all-electron mixed-basis approach as functions of frequency for Si in the cases of (a)  $G=G'=q=(0, 0, 0)$ , (b)  $G=G'=(1, 1, 1)$ ,  $q=(0, 0, 0)$  and (c)  $G=(1, 1, 1)$ ,  $G'=(2, 0, 0)$ ,  $q=(0, 0, 0)$ .

lectric response function for  $G=G'=(1, 1, 1)$  and  $q=(0, 0, 0)$ . At  $\omega=0$ , the calculated value for the real part of  $\epsilon$  is 1.8, which is a little larger than the pseudopotential results<sup>(3)(14)</sup>.  $\epsilon_2$  (imaginary part of  $\epsilon$ ) is zero at  $\omega=0$ . Both  $\epsilon_1$  and  $\epsilon_2$  are positive for all frequencies ( $0 < \omega < 50$  eV). These two curves have no sharp single-peak structure in  $\omega$  space like the case of Fig. 1(a). In  $t$  space this curve has a very sharp peak which indicates the response to a test charge is fast. Since the absolute value for all frequencies are smaller than the case of Fig. 1(a), the screening effect is weaker.

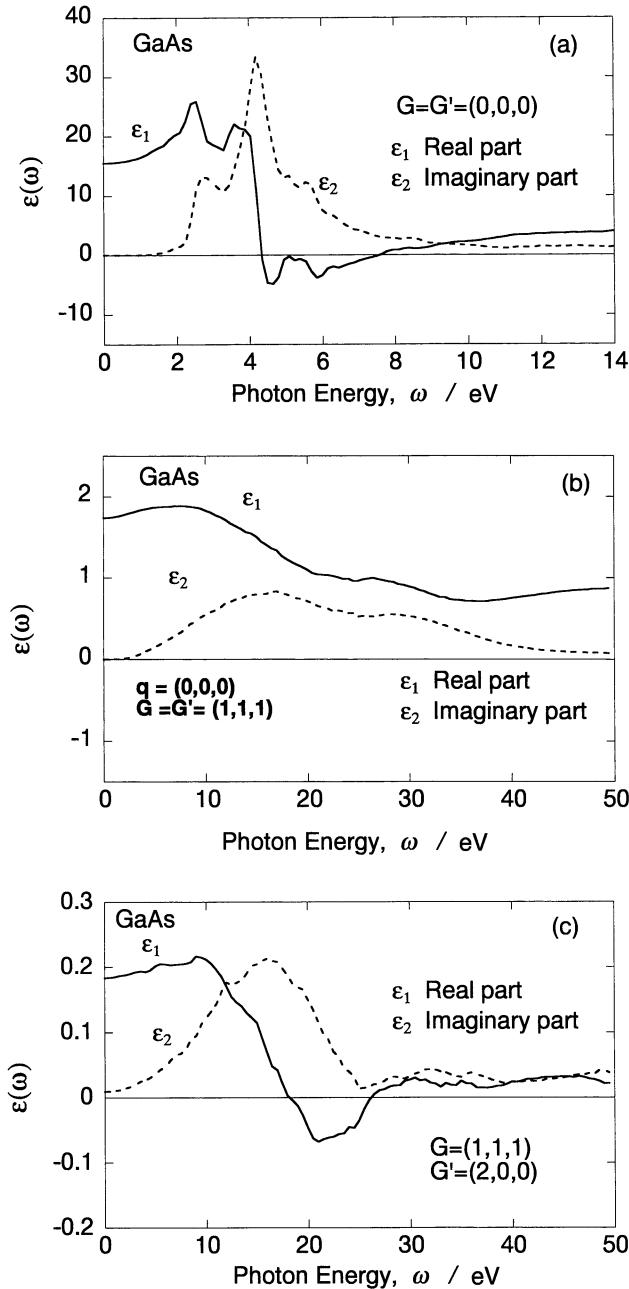


Fig. 2 Same as Fig. 1 except for GaAs, in the cases of (a)  $G=G'=q=(0,0,0)$ , (b)  $G=G'=(1,1,1)$ ,  $q=(0,0,0)$  and (c)  $G=(1,1,1)$ ,  $G'=(2,0,0)$ ,  $q=(0,0,0)$ .

Figure 1(c) shows frequency dependence of the dielectric response function for  $G=(1,1,1)$ ,  $G'=(2,0,0)$  and  $q=(0,0,0)$ , *i.e.* a case of local-field effects involved. The present value for  $\epsilon_1$  at  $\omega=0$  is 0.18, which is a little larger than the value of Ref. (3) and a little smaller than the value of Ref. (14).  $\epsilon_2$  at  $\omega=0$  is zero. The behaviours of  $\epsilon_1$  and  $\epsilon_2$  are also broad as in the case of Fig. 1(b), hence the response to a test charge is fast. Real part is an order of 0.1 at any frequency. Therefore screening effect is weaker than that of the previous cases.  $\epsilon_2$  is positive for  $0 < \omega < 30$  eV and then decreases to negative values as frequency increases.

We have checked core-electrons contribution in Si.

Core-levels contribution to the static dielectric constant is 1.0. In the cases of Fig. 1(b) and (c), core electrons do not contribute to the results. the core-electrons effects to the local field are negligible in Si.

We have also calculated and show in Fig. 2 the dielectric response function for GaAs. In evaluating the matrix elements of the eq. (3), we have omitted the effects of the d electrons. We have thus ignored the effects of core electrons. The d-electrons effects will be discussed elsewhere.

The value of our static dielectric constant  $\epsilon(q=0, \omega=0)$  in the case of  $G=G'=(0,0,0)$  is 15.5, and is larger than the experimental value 12.9<sup>(15)-(17)</sup> due to the same reason as for Si. As the frequency increases up to 1.5 eV (energy gap at  $\Gamma$ -point), the imaginary part becomes zero and the real part increases to about 28. At  $\omega \approx 4.5$  eV the real part changes sign from plus to minus, and then increases slowly to zero at  $\omega \approx 7.5$  eV as frequency increases. Up to  $7.5 < \omega < 15$  eV the imaginary part converges to 4.0.

Figure 2(b) shows the estimated frequency dependence of the dielectric function for  $G=G'=(1,1,1)$  and  $q=(0,0,0)$ . These two curves have no single-peak structure like the case of Fig. 1(b), and therefore it takes shorter time needed for the induced charge to response a test charge. Since the absolute value is smaller than the case of Fig. 2(a), the screening effect is weaker. The real part at  $\omega=0$  is about 1.7, and the imaginary part is zero. Both the real and imaginary parts are positive at any frequencies,  $0 < \omega < 50$  eV.

Figure 2(c) shows the frequency dependence of the dielectric response function for  $G=(1,1,1)$ ,  $G'=(2,0,0)$  and  $q=(0,0,0)$ , *i.e.* a case of local-field effects included as in the case of Si. At  $\omega=0$  the value of the real part is 0.18 and the imaginary part is almost zero. The real part is an order of 0.1 at any frequencies, so that the screening effect is judged to be weaker than the previous cases. These curves are also broad as in the case of Fig. 1(b), and the response to a test charge is fast. The imaginary part is positive for all frequencies at  $0 < \omega < 50$  eV.

#### IV. Conclusion

We have calculated dielectric response functions for Si and GaAs by our all-electron approach. The present results for Si are almost the same as the pseudopotential calculations<sup>(4)</sup>. Core contribution to the static dielectric constant is small for Si. For Si and GaAs the tendencies of the dielectric response functions depending on frequency are in good agreements with experiments except for the main-peak position in the case of  $q=G=G'=(0,0,0)$  because of inaccuracy of the LDA. Local-field effects are small but not negligible and responses in short-range are fast for Si and GaAs. Core electrons contribution to the local-field is negligible in Si. Within the LDA the amount of the gap energy is generally underestimated. This effect results in the slight underestimation of the static dielectric constant and also in the underestimation of the turning on point of the imaginary

part of the dielectric function as a function of the frequency. Although the present calculations were performed within the LDA, they can be used for a more sophisticated calculation involving the self-energy correction, of such as the *GW* approximation, in which the screened interaction with local-field effect plays an essential role. Such a calculation is now under progress, and will be published elsewhere<sup>(18)</sup>.

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