Evaluation of quasiparticle energies for semiconductors without inversion symmetry

S. B. Zhang,* D. Tománek,† Marvin L. Cohen, and Steven G. Louie
Department of Physics, University of California, Berkeley, California 94720
and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Mark S. Hybertsen
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974-2070
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We have generalized the Fourier-space Hybertsen-Louie self-energy approach for quasiparticle energies in semiconductors to cases without inversion symmetry. In the evaluation of the self-energy operator, a complex four-dimensional Fourier space is used to carry out the double Fourier transforms for time and spatial variables independently. The generalized plasmon-pole scheme for including both local fields and dynamical effects is also properly extended to systems without an inversion center. The quasiparticle energies for GaAs and AlAs are calculated with use of this approach and results in agreement with experimental data are obtained.

I. INTRODUCTION

Although the Hohenberg-Kohn-Sham local-density approximation (LDA) has been extensively and successfully used for many physical properties of solids, this theory encounters major difficulties when applied to the calculation of energy band gaps. One of the difficulties arises from the intrinsic limitation of the Kohn-Sham formulation of the density-functional theory[1] (DFT) where the ground-state properties are given accurately but the eigenvalues obtained using this theory have little direct physical meaning. The Kohn-Sham band gap is generally smaller than the true band gap by a finite amount attributed to the discontinuity in the exchange-correlation potential for adding an electron to the system.[2,3] This discontinuity is in general substantial. Moreover, owing to the $\mathbf{k}$ dependence of the electronic self-energy, a simple treatment such as the "scissors operator" approach which just enlarges the fundamental gap is inadequate.[4,5] In the LDA calculation, the exchange-correlation potential V_{xc} is further replaced by a local-density operator[6] which eliminates nonlocal effects.

To calculate the band gap correctly, one approach is to compute the ground-state energies for the N- and the $(N+1)$-particle systems using Jastrow-Slater-type trial wave functions. The excitation energies can then be obtained from total-energy differences.[7–10] An alternative approach, employed here, is to use the quasiparticle concept based on the Green's-function approach.[11] The quasiparticles are defined within the context of a one-particle Green's function such that each peak in the spectral function which is sufficiently sharp defines a quasiparticle energy. The quasiparticle approach allows a direct computation of the exchange-correlation contribution to the electron excitation energy and is hence comparatively simple. It provides insight into the screening behavior of the many-body system and the renormalization of quasiparticle properties. For an inhomogeneous system, the quasiparticle energies and wave functions are obtained by solving

$$(T+V_{\text{ext}}+V_h)\Psi_{n\mathbf{k}}(\mathbf{r}) + \int d^3r'\,\Sigma(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}')=E_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r})\,, \quad (1)$$

where T is the kinetic energy operator, V_{ext} is the external potential due to the ions, V_h is the average Coulomb or Hartree potential of the electrons, and Σ is the electron self-energy operator. The many-body effects of exchange and correlation among electrons are contained in Σ which is in general a nonlocal, energy-dependent, non-Hermitian operator. Hence the eigenvalue in Eq. (1), $E_{n\mathbf{k}}$, is complex, and its imaginary part gives the lifetime of the quasiparticle.

Recently, various approximations have been made to carry out the calculation for Σ.[4,5,12–15] Here, we will adopt the Hybertsen and Louie approach[4] which uses the Hedin GW approximation with dynamical screening and includes local-field effects. A generalized plasmon-pole approximation is used for the screened Coulomb interaction W. This approach has been successfully applied to determine the band structures for the bulk materials diamond, Ge, Si, and LiF,[4] for As adatoms on Ge and Si surfaces,[16] and for the Ge/Si interface[17] with an overall accuracy of 0.1–0.2 eV for the band gaps. Subsequently, a similar approach was taken by Godby *et al.*[5] using a method for evaluating W by a finite sampling at the imaginary-frequency axis and by von der Linden and Horsch[15] using empirical pseudopotentials with W obtained using plasmon poles given by the eigenvalues of the static dielectric matrix.

In this paper, we will extend the Hybertsen-Louie scheme to semiconductors without an inversion center and apply it to bulk GaAs and AlAs. Applications of the method to the GaAs-AlAs interfaces and superlattices have also been performed and will be discussed in a subsequent paper. This paper is organized as follows. In Sec. II, we review the Green's-function approach and the GW approximation. In Sec. III, the dynamically screened Coulomb interaction W and the generalized plasmon-pole model for systems without inversion sym-

metry are discussed. The computational details are given in Sec. IV and this approach is applied to the calculation of band gaps for GaAs and AlAs in Sec. V. Section VI contains a brief summary.

II. GREEN'S FUNCTION AND *GW* APPROXIMATION

In the framework of the Green's-function approach, particlelike excitations in an N-particle system are governed by the quasiparticle equation, Eq. (1), via Dyson's equation. The detailed formalism of the quasiparticle theory for electron systems has been discussed in the review of Hedin and Lundqvist.[11]

Our goal is to evaluate Σ in Eq. (1). However, Σ is related to the interacting Green's function G, the dynamically screened Coulomb interaction W, the irreducible polarizability P, and the vertex function Γ, $\Gamma=1+\delta\Sigma/\delta V$, where V is the total average potential. These quantities need to be evaluated in a self-consistent fashion. The approach of Hedin[12] which is adopted here is to generate for Σ a perturbation series in W. The first term in the series expansion so generated with respect to W is the GW approximation (i.e., $\Sigma=iGW$) where vertex corrections are neglected ($\Gamma=1$). Since G is the dressed Green's function and W is the screened Coulomb interaction, this procedure has a special advantage. The first-order term already contains part of the infinite expansion in terms of the bare Green's function and bare Coulomb interaction which yields a better convergence. In energy space, the explicit form for Σ is

$$\Sigma(\mathbf{r},\mathbf{r}';E)=i\int\frac{dE'}{2\pi}e^{-i\delta E'}G(\mathbf{r},\mathbf{r}';E-E')W(\mathbf{r},\mathbf{r}';E')\ , \tag{2}$$

where $\delta=0^+$ and

$$W(\mathbf{r},\mathbf{r}';E)=\int d^3r''\,\epsilon^{-1}(\mathbf{r},\mathbf{r}'';E)v(\mathbf{r}'',\mathbf{r}')\ , \tag{3}$$

with the bare Coulomb potential $v(\mathbf{r}'',\mathbf{r}')=e^2/|\mathbf{r}''-\mathbf{r}'|$ and ϵ^{-1} is the time-ordered dielectric screening function.

For nonmagnetic systems with time-reversal symmetry, both $\Psi_{n\mathbf{k}}(\mathbf{r})$ and its complex conjugate, $\Psi^*_{n\mathbf{k}}(\mathbf{r})$, are solutions of Eq. (1) with the same energy, E. Hence, a real eigenfunction corresponding to this eigenenergy can always be constructed to reduce the evaluation of the quasiparticle excitation spectrum to an evaluation of the real part of the generally complex energy E or, equivalently, to the expectation value for the real part of Σ. To examine the physical meaning of Σ, we decompose Σ into two terms,

$$\Sigma=\Sigma_{sex}+\Sigma_{coh}\ , \tag{4}$$

where the first term is given by the real part of the Green's function times the real part of the screened Coulomb interaction and the second term is from the product of the two corresponding imaginary parts and integrated over an internal energy variable. The screened exchange part, Σ_{sex}, arises from the poles of the Green's function, and the Coulomb-hole part, Σ_{coh}, from the poles of the screened interaction W. A detailed discussion for Σ_{sex} and Σ_{coh} is given in Ref. 4 in terms of the spectral functions for G and W.

The Green's function can be constructed from the quasiparticle wave functions and eigenenergies. These quasiparticle wave functions $\Psi_{n\mathbf{k}}(\mathbf{r})$ form a complete set of functions which in principle could be nonorthogonal. The explicit expression for the Green's function is

$$G(\mathbf{r},\mathbf{r}';E)=\sum_{n,\mathbf{k}}\frac{\Psi_{n\mathbf{k}}(\mathbf{r})\Psi^*_{n\mathbf{k}}(\mathbf{r}')}{E-E_{n\mathbf{k}}-i\delta_{n\mathbf{k}}}\ , \tag{5}$$

where $\delta_{n\mathbf{k}}=0^+$ for $E_{n\mathbf{k}}<E_F$; $\delta_{n\mathbf{k}}=0^-$ for $E_{n\mathbf{k}}>E_F$ and E_F is the Fermi energy. The quasiparticle energy is, in general, complex. In the following calculation, however, we neglect the imaginary part and approximate the spectral function by δ functions on the real axis. This is a reasonable approximation for quasiparticles near the Fermi level with long lifetimes.

There are two important aspects of the GW approximation—the local-field effect from the nonlocality of the screened Coulomb interaction and the dynamical screening effect from the energy dependence of the self-energy operator. Both effects are omitted in LDA calculations. In our discussions we concentrate to a large extent on how these effects give rise to results differing from the LDA calculations. For this reason, we will express the quasiparticle energy as the corresponding LDA value plus a correction from a many-body correction term, $\Sigma(E_{n\mathbf{k}})-V_{xc}^{LDA}$. Hence,

$$E_{n\mathbf{k}}=\epsilon_{n\mathbf{k}}^{LDA}+\frac{\langle\psi_{n\mathbf{k}}|\Sigma(E_{n\mathbf{k}})-V_{xc}^{LDA}|\Psi_{n\mathbf{k}}\rangle}{\langle\psi_{n\mathbf{k}}|\Psi_{n\mathbf{k}}\rangle}\ , \tag{6}$$

where $V_{xc}^{LDA}(\mathbf{r})$ is the LDA exchange-correlation potential and $\psi_{n\mathbf{k}}$ is the LDA wave function. Numerically, we find that the quasiparticle wave functions are very close to their LDA counterparts. If one expands the quasiparticle wave function in terms of the LDA wave functions, the higher-order terms in the resultant expansion of Eq. (6) will be negligible. The many-body correction, which is the second term in Eq. (6), can therefore be replaced by its first-order term, $\langle\psi_{n\mathbf{k}}|(\Sigma-V_{xc}^{LDA})|\psi_{n\mathbf{k}}\rangle$.

III. DYNAMICALLY SCREENED INTERACTION

The calculation of the screened Coulomb interaction W requires the full dielectric matrix $\epsilon^{-1}(\mathbf{r},\mathbf{r}';E)$ which has separate dependences on the spatial variables $\mathbf{r}$ and $\mathbf{r}'$. As mentioned earlier, this leads to local-field effects, i.e., the screening varies on an atomic scale due to the charge inhomogeneity in semiconductors. The screened interaction W is given by the time-ordered dielectric matrix ϵ^{-1} via Eq. (3). The time-ordered dielectric matrix is further related to the linear-response retarded dielectric matrix—their real parts are the same but their imaginary parts differ by a sign for negative frequencies. Our strategy is to calculate as accurately as possible the static dielectric matrix $\epsilon^{-1}(\mathbf{r},\mathbf{r}';E=0)$. Then we use the analytic properties of the retarded dielectric matrix to obtain a generalized plasmon-pole model which approximates the screening and the screened Coulomb interaction W at finite frequencies.

A. Spatial Fourier transformation and static dielectric matrix

In our approach, the quasiparticle calculation [i.e., the solution of Eq. (1)] will be carried out in Fourier space, which is the obvious choice for periodic systems. The dielectric matrix should also be formulated in the same space. Our convention for the Fourier transform is

$$W(\mathbf{r},\mathbf{r}';\omega)=\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'} e^{j(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} W_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) e^{-j(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} , \quad (7)$$

where $j=\sqrt{-1}$, ω is the energy variable, $\mathbf{G}$ is a reciprocal lattice vector, $\mathbf{q}$ is a wave vector in the first Brillouin zone, and

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)=\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) v(\mathbf{q}+\mathbf{G}') . \quad (8)$$

Before taking the Fourier transform, any function g in this formalism is considered as a scalar function with real-space variables, $\mathbf{r}$ and $\mathbf{r}'$, and a time variable t. The spatial Fourier transform is considered independent of the Fourier transform of the time variable. Each transform brings the function g into a two-dimensional space,

$$\begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix} .$$

Therefore, the double Fourier transforms of function g are equivalent to a direct product of two 2×2 matrices,

$$\begin{bmatrix} 1 & 0 \\ 0 & j \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix} .$$

Hence, the Fourier components of the doubly transformed function g are defined on the four-dimensional space spanned by $(1,j,i,ij)$ where the imaginary number j is used for spatial variables in order to avoid confusion with the imaginary number i used for the time variable t. The real and imaginary parts resulting from the usual time transform of the function g will be denoted by subscripts 1 and 2 and both will have real and imaginary spatial Fourier components. The case in which the system has inversion symmetry is a special case where the spatial Fourier transform is real and the four-dimensional space is reduce to two dimensions.

The time Fourier-transformed random-phase-approximation (RPA) irreducible polarizability (the independent particle polarizability) P is defined as

$$P(\mathbf{r},\mathbf{r}';\omega)=-i\int \frac{d\omega'}{2\pi} e^{-i\delta\omega'} G(\mathbf{r},\mathbf{r}';\omega-\omega') G(\mathbf{r}',\mathbf{r};\omega') , \quad (9)$$

where $\delta=0^+$. The dielectric matrix $\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$ in the RPA is related to the polarizability P by

$$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)=\delta_{\mathbf{G}\mathbf{G}'}-v(\mathbf{q}+\mathbf{G})P_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) . \quad (10)$$

Since the static dielectric matrix is a ground-state property, our calculation for the static polarizability can be performed within the LDA approximation via the Adler-Wiser formalism,[18]

$$P_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega=0)=\sum_{n,n',\mathbf{k}} \frac{f(\varepsilon_{n',\mathbf{k}+\mathbf{q}})-f(\varepsilon_{n\mathbf{k}})}{\varepsilon_{n',\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}} \times\langle\psi_{n\mathbf{k}}|e^{-j(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{n',\mathbf{k}+\mathbf{q}}\rangle \times\langle\psi_{n',\mathbf{k}+\mathbf{q}}|e^{j(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|\psi_{n\mathbf{k}}\rangle , \quad (11)$$

where $f(\varepsilon)$ denotes the fermion occupation factors and ε denotes the LDA eigenvalues. From Eqs. (10) and (11), the static dielectric matrix is computed as outlined previously[19] and inverted to give $\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega=0)$. To obtain the ω-dependent dielectric matrix, we made use of a generalized plasmon-pole model given in the following section.

B. Generalized plasmon-pole model

The use of the generalized plasmon-pole (GPP) model is based on the physical observation that $\epsilon^{-1}_{2,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$, the imaginary part of the time-Fourier-transformed inverse dielectric function ϵ^{-1}, is generally a peaked function of ω. Accordingly, one may approximate the time-ordered ϵ^{-1}_2 by

$$\epsilon^{-1}_{2,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)=A_{\mathbf{G}\mathbf{G}'}(\mathbf{q})[\delta(\omega-\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})) -\delta(\omega+\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}))] , \quad (12)$$

where A and $\tilde{\omega}$ are the amplitude and frequency for the plasmon poles, respectively. For cases where there is not a well-defined single peak, direct calculations showed that $\epsilon_{2,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$ tends to be small and fluctuates in sign as a function of ω.[4] Equation (12) suggests that A can be complex for systems without inversion symmetry but $\tilde{\omega}$ should be real. In Ref. 4, A and $\tilde{\omega}$ are determined from the Kramers-Kronig relations[20] and the generalized version of the Johnson f-sum rules[21] derived for the retarded dielectric matrices. It can be shown that these relations and sum rules also hold for systems without inversion symmetry as long as these systems are nonmagnetic. Hence,

$$\epsilon^{-1}_{1,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega=0)=\delta_{\mathbf{G}\mathbf{G}'}+\frac{2}{\pi}\mathrm{P}\int_0^\infty d\omega\frac{1}{\omega}\epsilon^{-1}_{2,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) , \quad (13)$$

and

$$\int_0^\infty d\omega\,\omega\epsilon^{-1}_{2,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) =-\frac{\pi}{2}\omega_p^2\frac{(\mathbf{q}+\mathbf{G})\cdot(\mathbf{q}+\mathbf{G}')}{|\mathbf{q}+\mathbf{G}|^2}\frac{\rho(\mathbf{G}-\mathbf{G}')}{\rho(0)} , \quad (14)$$

where $\rho(\mathbf{G})$ is the Fourier transform of the ground-state charge density and ω_p is the classical plasma frequency. Since Eqs. (13) and (14) are given for frequency ranges in which the time-ordered and the retarded dielectric matrices are identical, no distinction has been made between the two.

We note that Eq. (13), the Kramers-Kronig relation, connects the inverse frequency moment of ϵ^{-1}_2 to the static ϵ^{-1}_1 whereas Eq. (14), the generalized f-sum rule, relates the first moment of ϵ^{-1}_2 to the ground-state charge density. This set of coupled equations in general cannot be satisfied by Eq. (12), the single-plasmon-pole approxi-

mation for ϵ_2^{-1} with the requirement that $\tilde{\omega}$ is real. The physical reason is that the static linear response and the spatial-charge distribution are different physical quantities and could be spatially out of phase. In another word,

$$\mathrm{Im}\left[\frac{\rho(\mathbf{G}-\mathbf{G}')}{\epsilon^{-1}_{1,\mathbf{GG}'}(\mathbf{q},\omega=0)}\right]\neq 0 .$$

It is important to realize that the high-frequency components of ϵ_2^{-1}, although small, give finite contributions to the generalized f-sum rule, Eq. (14), because of the increasing weighting factor of ω as $\omega\rightarrow\infty$. Hence, the low-frequency components of ϵ_2^{-1} generally cannot be separated from the high-frequency components in Eq. (14), which makes it difficult to use a single-pole approximation. It is, however, not the case for the Kramers-Kronig relation since in this case, the weighting factor is $1/\omega$. To handle these difficulties, we use a minimal two-δ function approximation for ϵ_2^{-1} and keep the high-frequency term in Eq. (14). The δ function which contributes to the self-energy calculation is, however, solely the low-frequency one corresponding to the usual plasmon pole.

Hence, we write

$$\epsilon^{-1}_{2,\mathbf{GG}'}(\mathbf{q},\omega)=\{A_{\mathbf{GG}'}(\mathbf{q})[\delta(\omega-\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q}))-\delta(\omega+\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q}))]+B_{\mathbf{GG}'}(\mathbf{q})[\delta(\omega-\tilde{\omega}'_{\mathbf{GG}'}(\mathbf{q}))-\delta(\omega+\tilde{\omega}'_{\mathbf{GG}'}(\mathbf{q}))]\}\Omega^2_{\mathbf{GG}'}(\mathbf{q}) , \tag{15}$$

where

$$\Omega^2_{\mathbf{GG}'}(\mathbf{q})=\omega_p^2\frac{(\mathbf{q}+\mathbf{G})\cdot(\mathbf{q}+\mathbf{G}')}{|\mathbf{q}+\mathbf{G}|^2}\frac{\rho(\mathbf{G}-\mathbf{G}')}{\rho(\mathbf{0})} . \tag{16}$$

We then define

$$\frac{\Omega^2_{\mathbf{GG}'}(\mathbf{q})}{\delta_{\mathbf{GG}'}-\epsilon^{-1}_{1,\mathbf{GG}'}(\mathbf{q},\omega=0)}=\lambda_{\mathbf{GG}'}(\mathbf{q})e^{j\phi_{\mathbf{GG}'}(\mathbf{q})} , \tag{17}$$

where $\lambda_{\mathbf{GG}'}(\mathbf{q})>0$. Combining Eq. (15) with Eqs. (13) and (14), the following coupled equations are obtained,

$$\frac{A_{\mathbf{GG}'}(\mathbf{q})}{\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})}+\frac{B_{\mathbf{GG}'}(\mathbf{q})}{\tilde{\omega}'_{\mathbf{GG}'}(\mathbf{q})}=-\frac{\pi}{2}\frac{e^{-j\phi_{\mathbf{GG}'}(\mathbf{q})}}{\lambda_{\mathbf{GG}'}(\mathbf{q})} , \tag{18}$$

and

$$A_{\mathbf{GG}'}(\mathbf{q})\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})+B_{\mathbf{GG}'}(\mathbf{q})\tilde{\omega}'_{\mathbf{GG}'}(\mathbf{q})=-\tfrac{1}{2}\pi . \tag{19}$$

Equations (18) and (19) are solved subject to the symmetry requirements on ϵ_2^{-1} for A and $\tilde{\omega}$ under the conditions that $\tilde{\omega}'\rightarrow\infty$ but $B\tilde{\omega}'$ remains finite. This yields

$$\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})=\left[\frac{\lambda_{\mathbf{GG}'}(\mathbf{q})}{\cos[\phi_{\mathbf{GG}'}(\mathbf{q})]}\right]^{1/2} , \tag{20}$$

and

$$A_{\mathbf{GG}'}(\mathbf{q})=-\frac{\pi}{2}\frac{e^{-j\phi_{\mathbf{GG}'}(\mathbf{q})}}{\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q})\cos[\phi_{\mathbf{GG}'}(\mathbf{q})]} . \tag{21}$$

There are no adjustable parameters used in this generalized plasmon-pole model. More general features for the model have been discussed in Ref. 4.

Recently, von der Linden and Horsch[15] proposed a different scheme for applying the plasmon-pole approximation, i.e., utilizing the diagonal representation of $\epsilon^{-1}_{1,\mathbf{GG}'}(\mathbf{q},\omega=0)$.[22] This scheme has the advantage of avoiding the possible imaginary solution of Eq. (20). Only N poles are used where N is the dimension of the static dielectric matrix. This model, however, suffers from the difficulty that in general $\epsilon_1^{-1}(\mathbf{q},\omega=0)$ and $\Omega^2_{\mathbf{GG}'}(\mathbf{q})$ cannot be simultaneously diagonalized so that all the off-diagonal terms of $\Omega^2_{\mathbf{GG}'}(\mathbf{q})$ after the diagonalization procedure have to be omitted. For systems without inversion symmetry, this would imply no phase difference between the static inverse dielectric matrix and the charge density, which is probably not a bad approximation for GaAs but could be less accurate for materials with larger ionicities. A more optimal scheme without the drawbacks of the above two models was recently developed and will be discussed elsewhere.[23] Nevertheless, the evaluation of the self-energy operator generally involves a sum over frequencies in the screened Coulomb interaction, and usually the fine details of the frequency dependence are not important.

IV. COMPUTATIONAL DETAILS

We use *ab initio* pseudopotentials[24] in the scalar-relativistic form[25] which greatly simplify the calculations. However, this approach introduces small error because of the improper treatment of the core-valence exchange and the core-polarization contribution to Σ using a LDA frozen core. The errors for GaAs and AlAs are somewhat larger than those for Si because of the relatively larger cores of Ga and Al, and the softer core of Ga. But the results should be comparable to Ge.[4] The size of these effects has been estimated using atomic calculations to be about 0.3 eV for transitions between states having pure p character and pure s character. This extreme case corresponds to the minimum direct gap in Ge.

To calculate the quasiparticle energies, Eq. (1) is converted into matrix form by expansion of the quasiparticle wave functions using the LDA basis. Initially, the wave functions and eigenvalues are calculated by approximating Σ by the LDA Green's functions and the screened Coulomb interaction W given by the GPP model. The Green's functions and the Hartree potentials in Eq. (1) in principle should be updated iteratively to self-consistency. We, however, use the fact that the LDA wave functions are almost identical to the quasiparticle wave functions so that updating the wave functions are unnecessary. Hence, only the quasiparticle energies in the Green's functions [Eq. (5)] are updated. The errors in replacing the quasiparticle wave functions by the LDA

wave functions have been estimated to be less than a few hundredth of an eV. Therefore, Eq. (6) can be approximated by

$$E_{n\mathbf{k}}=\varepsilon_{n\mathbf{k}}^{\mathrm{LDA}}+\langle\psi_{n\mathbf{k}}|\Sigma(E_{n\mathbf{k}})|\psi_{n\mathbf{k}}\rangle-\langle\psi_{n\mathbf{k}}|V_{\mathrm{xc}}^{\mathrm{LDA}}|\psi_{n\mathbf{k}}\rangle \tag{22}$$

with

$$\langle\psi_{n\mathbf{k}}|\Sigma(E)|\psi_{n\mathbf{k}}\rangle=\langle\psi_{n\mathbf{k}}|\Sigma_{sex}(E)|\psi_{n\mathbf{k}}\rangle+\langle\psi_{n\mathbf{k}}|\Sigma_{\mathrm{coh}}(E)|\psi_{n\mathbf{k}}\rangle\ , \tag{23}$$

where

$$\langle\psi_{n\mathbf{k}}|\Sigma_{sex}(E)|\psi_{n\mathbf{k}}\rangle=-\sum_{n_1}^{\mathrm{occ}}\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\left[\delta_{\mathbf{G}\mathbf{G}'}+\frac{\Omega^2_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\{1-j\tan[\phi_{\mathbf{G}\mathbf{G}'}(\mathbf{q})]\}}{(E-E_{n_1,\mathbf{k}-\mathbf{q}})^2-\tilde{\omega}^2_{\mathbf{G}\mathbf{G}'}(\mathbf{q})}\right]v(\mathbf{q}+\mathbf{G}')$$
$$\times\langle\psi_{n\mathbf{k}}|e^{j(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{n_1,\mathbf{k}-\mathbf{q}}\rangle\langle\psi_{n_1,\mathbf{k}-\mathbf{q}}|e^{-j(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|\psi_{n\mathbf{k}}\rangle\ , \tag{24}$$

and

$$\langle\psi_{n\mathbf{k}}|\Sigma_{\mathrm{coh}}(E)|\psi_{n\mathbf{k}}\rangle=\tfrac{1}{2}\sum_{n_1}\sum_{\mathbf{q},\mathbf{G},\mathbf{G}'}\frac{\Omega^2_{\mathbf{G}\mathbf{G}'}(\mathbf{q})\{1-j\tan[\phi_{\mathbf{G}\mathbf{G}'}(\mathbf{q})]\}}{\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})[E-E_{n_1\mathbf{k}-\mathbf{q}}-\tilde{\omega}_{\mathbf{G}\mathbf{G}'}(\mathbf{q})]}v(\mathbf{q}+\mathbf{G}')$$
$$\times\langle\psi_{n\mathbf{k}}|e^{j(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_{n_1,\mathbf{k}-\mathbf{q}}\rangle\langle\psi_{n_1,\mathbf{k}-\mathbf{q}}|e^{-j(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}|\psi_{n\mathbf{k}}\rangle\ . \tag{25}$$

The LDA calculations are carried out using a plane-wave basis with energy cutoffs of 16 Ry for the Hamiltonian and 64 Ry for the charge densities for GaAs and AlAs. These cutoffs are chosen to ensure convergence of the LDA spectrum (the direct gaps are converged to within 0.02 eV). Summations over the Brillouin zone for the LDA charge density and potentials were performed using a 10-special-point scheme.[26] In some cases, the Ceperley-Alder exchange-correlation potential[27] is used, although, in principle, the von Barth and Hedin correlation energy[28] should be used to be consistent with the RPA approximation for Σ. This has no effect on band gaps and excitation energies since the difference is just a constant shift of the quasiparticle energies relative to the reference LDA eigenvalues.[4]

The sum over *Umklapp* process $\mathbf{G}$ and $\mathbf{G}'$ in Eqs. (24) and (25) requires a cutoff $G_{\max}$ so that $|\mathbf{q}+\mathbf{G}|\le G_{\max}$. In the calculation of Σ for GaAs and AlAs, $G^2_{\max}=9$ Ry, and 100 lowest bands for n_1 are used. The sum over the irreducible Brillouin zone for Σ is carried out at several different sets of q points (3,10,14) including $\mathbf{q}=0$ and the results are found to be converged for 10 q points. We estimate that the final results for the *GW* quasiparticle energies are converged to within a few hundredths of an eV for the above cutoffs. The special treatment for the static dielectric matrix for $\mathbf{q}\to 0$ follows the method outlined in Ref. 4.

V. GaAs AND AlAs BAND GAPS

In the calculation of quasiparticle energy gaps for bulk GaAs and AlAs, experimental values for the crystal volumes[29] were used. The *GW* quasiparticle energies for the high-symmetry points, Γ, X, and L, are summarized in Table I for GaAs and Table II for AlAs. The spin-orbit splittings were calculated using the first-order perturbation as outlined in Ref. 30. These splittings are in good agreement with the experimental data.[29]

The *GW* quasiparticle calculation provides a dramatic improvement over the LDA results for the band gaps. Compared with the experimental values, most of the results agree to within $\sim$0.2 eV. In contrast, the LDA values can be in error by more than 1 eV and are consistently too small. The gap between the Γ and L minima for AlAs has not been measured directly. A recent *GW* quasiparticle calculation[31] predicted that this gap is 3.03 eV. Our present value, 2.79 eV, is smaller but in better agreement with the value extrapolated from alloy data, 2.54 eV.[32] The largest discrepancy between the quasipar-

TABLE I. LDA eigenvalues, present *GW* quasiparticle energies, and many-body corrections ($\delta=E^{\mathrm{qp}}-\epsilon^{\mathrm{LDA}}$) for GaAs in eV. Spin-orbit splittings are included. Experimental energy gaps are given by Ref. 29. Quasiparticle energies and many-body corrections from Ref. 31 [Godby, Schlüter, and Sham (GSS)] are also included.

Methods	Γ_{15v}	Γ_{1c}	X_{5v}	X_{1c}	L_{3v}	L_{1c}	Γ_{15v}-Γ_{1c}	X_{5v}-X_{1c}	L_{3v}-L_{1c}
LDA	0.0(−0.34)	0.38	−2.71(−2.79)	1.32	−1.16(−1.37)	0.88	0.38	4.04	2.04
Present work	0.0(−0.34)	1.29	−2.79(−2.87)	2.05	−1.19(−1.40)	1.69	1.29	4.90	2.89
GSS[a]	0.0(−0.34)	1.47	−2.73(−2.80)	2.08	−1.11(−1.32)	1.82	1.47	4.81	2.93
Experiment	0.0(−0.34)	1.52	−2.78(−2.85)	2.01	−1.19(−1.40)	1.84	1.52	4.94	3.01
δ(present)	0.0	0.91	−0.08	0.73	−0.03	0.81			
δ(GSS)	0.0	0.91	−0.07	0.70	−0.04	0.78			

[a]Reference 31.

TABLE II. LDA eigenvalues, present *GW* quasiparticle energies, and many-body corrections ($\delta = E^{qp} - \epsilon^{LDA}$) for AlAs in eV. Spin-orbit splittings are included. Experimental energy gaps are given by Ref. 29. Quasiparticle energies and many-body corrections from Ref. 31 [Godby, Schlüter, and Sham (GSS)] are also included.

Methods	Γ_{15v}	Γ_{1c}	X_{5v}	X_{1c}	L_{3v}	L_{1c}	Γ_{15v}-Γ_{1c}	X_{5c}-X_{1c}	L_{3v}-L_{1c}
LDA	0.0(−0.30)	1.82	−2.21(−2.34)	1.28	−0.86(−1.04)	1.95	1.82	3.49	2.79
Present work	0.0(−0.30)	2.75	−2.35(−2.48)	2.08	−0.93(−1.11)	2.79	2.75	4.43	3.72
GSS[a]	0.0(−0.28)	3.26	−2.34(−2.49)	2.09	−0.88(−1.08)	3.03	3.26	4.43	3.91
Experiment	0.0(−0.28)	3.11	−2.30(−2.45)	2.24	−1.31(−1.51)	2.54[b]	3.11	4.54	3.80
δ(present)	0.0	0.93	−0.14	0.80	−0.07	0.84			
δ(GSS)	0.0	0.93	−0.13	0.81	−0.08	0.90			

[a]Reference 31.
[b]Reference 32.

ticle and the measured gaps is for the direct gap at Γ. This can be understood since the core corrections are largest for the pure *s*-like excited state as discussed earlier.[4] We note from these tables that the disagreement for the direct gap of AlAs is larger than that for GaAs. Since the minimum gap for AlAs is an indirect gap (Γ to *X*) and since the AlAs samples are hygroscopic and usually difficult to handle, we expect a larger uncertainty for the measured direct-gap value for AlAs. Our GPP model for evaluating the screened Coulomb interaction *W* is computationally simpler than the method used by Godby *et al.*[5] which samples *W* along the imaginary frequency axis. However, the many-body correction terms ($\delta = E^{qp} - \varepsilon^{LDA}$) shown in Tables I and II are still in agreement with those calculated by Godby *et al.*[31] to within a few hundredths of an eV. Hence, the scheme presented here can be applied to more complicated systems such as surfaces and interfaces. The quasiparticle gap values for Γ and *L* points are larger in Ref. 31 than in the present results. Their values are closer to the experimental values at Γ_{1c} and L_{1c} for GaAs and at Γ_{1c} for AlAs. We believe the agreement is somewhat fortuitous and the differences between the two sets of results arise from a difference in the convergence of the LDA eigenvalues ε^{LDA} in the two calculations. We found a 12 Ry energy cutoff, which is used in Ref. 31, is not large enough for convergent results for ε^{LDA} even though the many-body correction terms at this cutoff are already converged.

VI. SUMMARY

We have extended the Fourier-space Hybertsen-Louie quasiparticle self-energy approach to semiconductors without an inversion center by using a complex four-dimensional Fourier-space formalism. A generalized plasmon-pole scheme for including both local fields and dynamical effects is introduced. The quasiparticle energies and many-body corrections to the LDA eigenvalues for GaAs and AlAs are calculated using this approach and are in good agreement with the experimental data and other quasiparticle calculations.

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*Present address: Xerox Palo Alto Research Center, 3333 Coyote Hill Rd., Palo Alto, CA 94304.
†Present address: Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824-1116.

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