Theory of optical absorption in diamond, Si, Ge, and GaAs

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We report first-principles calculations of $\epsilon_2(\omega)$ for diamond, Si, Ge, and GaAs that include the electron-hole interaction in detail. The only essential experimental input is the crystal structure of the materials. Comparison with reflectivity and ellipsometry measurements allows us to assess the validity of the approximations made in the calculation. We conclude that the approximation of singly excited electronic states and a statically screened electron-hole interaction is sufficient to understand the main features of the absorption spectra of these materials in the visible to near ultraviolet. [S0163-1829(98)51416-6]

I. INTRODUCTION

Optical absorption in semiconductors and insulators has been studied extensively for many decades. Highly reproducible reflectivity and ellipsometry measurements have been performed on many materials commonly used in the semiconductor and optoelectronics industries.[1] Yet, until now, accurate first-principles calculations of absorption spectra have been lacking. This is because the description of optical absorption requires the inclusion of the electron-hole interaction,[2] which is responsible for the existence of exciton levels and enhancement of absorption features just above the mobility edge. Current state-of-the-art *ab initio* computations of optical properties involve quasiparticle calculations,[3] and a partial inclusion of dynamical vertex corrections[4] that neglect excitonic effects.

In this paper, we calculate $\epsilon_2(\omega)$ for four materials, diamond, Si, Ge, and GaAs, using an *ab initio* computational technique that includes the electron-hole interaction.[5] The electron-hole attraction shifts the oscillator strength to lower frequencies, bringing the theoretical results into, to the best of our knowledge, unprecedented agreement with experiment. From this, we learn that the major approximations made—a single-determinant ground state, singly excited electron-hole pair states, and static screening of the attraction—are sufficient to account for the main features in the absorption spectra of these materials in the visible to near ultraviolet. In what follows, we review the theoretical method, present our results, and discuss their implications.

II. THEORY

The frequency-dependent imaginary part of the dielectric function can be written as

$$\epsilon_2(\omega) = \frac{4\pi^2}{\omega^2} \sum_f |\langle 0|\hat{\boldsymbol{\lambda}}\cdot\mathbf{J}|f\rangle|^2 \delta(|\omega| - E_f), \qquad (1)$$

where $\hat{\boldsymbol{\lambda}}\cdot\mathbf{J}$ is the component of the macroscopic current-density operator along the polarization direction, $|0\rangle$ is the ground state of the solid, and the $\{|f\rangle\}$ are excited states. In our method,[5] $\epsilon_2(\omega)$ is calculated in the Haydock recursion scheme,[6] which entails iteratively acting with the Hamiltonian H to obtain spectral moments of $\hat{\boldsymbol{\lambda}}\cdot\mathbf{J}|0\rangle$. Individual states $\{|f\rangle\}$, and energies $\{E_f\}$ need not be computed.

The ground state $|0\rangle$ is taken to have a filled valence band. $\mathbf{J}$ creates an electron above the band gap, and a hole below, so $\hat{\boldsymbol{\lambda}}\cdot\mathbf{J}|0\rangle$ is a singly excited electronic state. H acts within the subspace of singly excited states, and has three terms:

$$H = H_{1e} + H_{ex} + H_{dir}. \qquad (2)$$

$H_{1e} = H_{el} + H_{hole}$ is the Hamiltonian for independent electrons and holes. Eigenstates of H_{el} and H_{hole} are taken to be pseudopotential local-density approximation (LDA) wave functions[7] but with LDA band energies corrected using a combination of quasiparticle calculations[3] and experiment.[8] H_{ex} and H_{dir} are the exchange and direct parts of the electron-hole interaction. H_{ex} is repulsive, while H_{dir} is attractive. We use the bare Coulomb interaction in H_{ex}, and the statically screened Coulomb interaction W in H_{dir}.[2,9] W is calculated with the Levine-Louie-Hybertsen model[10] using the LDA charge density and the experimental dielectric constant ϵ_∞.[11]

We use two different bases to represent the excited states: an $(i,j;\mathbf{k})$ basis, and an $(\mathbf{x},\mathbf{y};\mathbf{R})$ basis. The i and j are electron and hole band indices, and $\mathbf{k}$ is the hole wave vector (the electron wave vector is $\mathbf{k}+\mathbf{q}\approx\mathbf{k}$, where $\hbar\mathbf{q}$ is the photon momentum). The $\mathbf{x}$ and $\mathbf{y}$ are (real-space) positions of the electron and hole in their unit cells, and $\mathbf{R}$ is the lattice vector separating the cells. To simplify computation of the action of H on a state vector ψ, we act with each term of H in the basis in which it is diagonal. $H_{1e}\psi$ is computed in the $(i,j;\mathbf{k})$ basis, while $H_{dir}\psi$ is computed in the $(\mathbf{x},\mathbf{y};\mathbf{R})$ basis. $H_{ex}\psi$ is treated by standard reciprocal-space techniques. The relevant calculational parameters are $N_\mathbf{k}(=N_\mathbf{R})$, number of $\mathbf{k}$ points; $N_\mathbf{x}$, number of $\mathbf{x}$ and $\mathbf{y}$ points; N_v, number of valence bands; N_c, number of conduction bands; η, Lorentzian broadening parameter used to broaden the δ functions in Eq. (1); and N_{iter}, number of iterations (actions of H) used to determine $\epsilon_2(\omega)$.
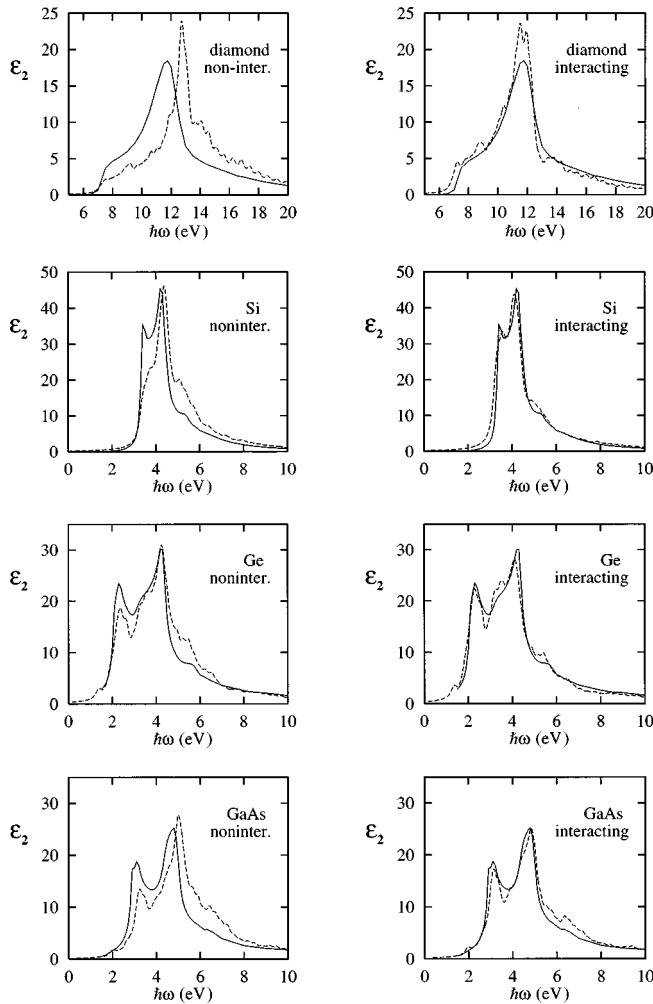
FIG. 1. $\epsilon_2(\omega)$ versus $\hbar\omega$ for diamond, Si, Ge, and GaAs. The left-hand column contains theoretical results neglecting the electron-hole interaction (dashed lines), and experimental results of Ref. 1 (solid lines). The right-hand column contains theoretical results including the electron-hole interaction (dashed), and the same experimental results (solid).

III. RESULTS AND DISCUSSION

We present results for four crystalline materials: diamond, Si, Ge, and GaAs. For all four, we have used $N_{\mathbf{k}} = 512$ ($8 \times 8 \times 8$ mesh), $N_{\mathbf{x}} = 27$ ($3 \times 3 \times 3$ mesh), $N_v = 4$, $N_c = 8$, and $N_{\text{iter}} = 100$. With these values, the calculated spectra are sufficiently converged to compare with experiment.[12] All results are presented in Fig. 1. Solid lines are from various experiments,[1] and dashed lines are our theoretical results. The left-hand column shows the results of one-electron theory, obtained by neglecting the electron-hole interaction [last two terms of Eq. (2)]. The right-hand column shows the results of the full calculation, which includes the electron-hole interaction. The broadening parameter η is chosen to be 0.2 eV [0.4 eV full-width at half maximum (FWHM)] for diamond, and 0.15 eV (0.3 eV FWHM) for Si, Ge, and GaAs. We used $\epsilon_\infty(\text{diamond}) = 5.5$, $\epsilon_\infty(\text{Si}) = 11.4$, $\epsilon_\infty(\text{Ge}) = 15.8$, and $\epsilon_\infty(\text{GaAs}) = 10.9$.

The generic feature of the one-electron theory is to place oscillator strength too high in energy relative to experiment.

This can be seen for all four solids in the left-hand column. The net attraction of the electron-hole interaction decreases the energy of the excited states, and moves oscillator strength to lower energies. This can be seen by comparing the noninteracting and interacting results. Note that the change is most pronounced for diamond, while noninteracting and interacting results are not very different for Ge. At long range the screened electron-hole interaction is approximately $e^2/[\epsilon_\infty r]$. Thus, the electron-hole interaction is large for insulators, and small for narrow-gap semiconductors. Note also that the Ge and GaAs spectra are very similar, because of the proximity of Ga and As to Ge in the periodic table. The pronounced effect of the electron-hole interaction in Si is probably a result of the highest valence and lowest conduction bands being nearly parallel throughout the Brillouin zone. In general, the agreement between the interacting theory and experiment is extremely good for the materials studied. To our knowledge, this represents the closest correspondence to date between *ab initio* theory of optical properties of solids and experiment. Some notable discrepancies between our theory and experiment include absorption edges of diamond and Si that are a few tenths of an eV too high in energy, and peak heights between 5 eV and 7 eV that are too large in Si, Ge, and GaAs.

The close correspondence between the interacting theory and experiment suggests that the approximations made are adequate in this context. One of the most drastic approximations is the complete neglect of lattice vibrations. Undoubtedly, phonons are responsible for broadening spectral features. The fact that the theory predicts relative peak heights well shows that the coupling of phonons to the excited electronic states is of secondary importance. Another major approximation is the neglect of multielectron excitations. This approximation should probably be worse for narrow-gap systems. The results show that, even for Ge, theory and experiment are in good agreement for energies greater than twice the band gap. Thus, multiply excited electronic states are not crucially important for understanding optical absorption in these materials. Finally, the static screening approximation for the direct part of the electron-hole interaction seems to be adequate. This is not surprising, because the plasma frequencies of these systems are well above the energies at which the absorption is large.

It is interesting to compare our results to prior predictions of $\epsilon_2(\omega)$ for the same materials. Diamond and Si spectra were predicted by Sham and Rice, and Hanke and Sham,[2] the first quantitative calculations of $\epsilon_2(\omega)$ to include the electron-hole attraction. These authors make the same approximations discussed above, but use an empirical tight-binding basis to represent the one-electron band states. Their diamond spectrum is very similar to our first-principles results. However, their Si spectrum is rather different: the peak near 3.5 eV is larger than the one near 4.2 eV, in contrast to our results and experiment. Bechstedt *et al.*[4] recently revisited the problem of $\epsilon_2(\omega)$ in diamond and Si, and showed that the dynamical quasiparticle corrections to the LDA (Ref. 3) are largely canceled by the use of dynamical vertex corrections. From this, they argue that using the ''bare LDA'' is better for the calculation of optical properties than the quasiparticle corrected results taken alone. While this is certainly true, the present approach includes both quasiparticle

corrections and the electron-hole attraction, producing spectra that are substantially closer to experiment than does the ''bare LDA.'' [13]

IV. CONCLUSIONS

We have presented results for the calculation of optical absorption in the visible and ultraviolet for four materials: diamond, Si, Ge, and GaAs. By including the electron-hole interaction in a first-principles framework, we obtain extremely good agreement between theory and experiment for $\epsilon_2(\omega)$. This shows that the approximations inherent in the theory are adequate for understanding the optical properties of these materials. Also, it opens up the possibility for predicting optical properties of new materials, and designing materials with desired optical properties.

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[8] Quasiparticle results yield ~ 0.1 eV accuracy for all materials treated, but experimental numbers are well established in these solids and have been used. Corrections include a rigid shift of unoccupied bands to realize the band gap, and a 6.4% stretch of the valence band in diamond [see Ref. 3; for diamond, see also I. Jiménez *et al.*, Phys. Rev. B **56**, 7215 (1997)].

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[11] Just as for quasiparticle energies, the calculated ϵ_∞ is sufficiently accurate, but the known ϵ_∞ was used.

[12] A 512-point sampling of the Brillouin zone is found to be adequately converged, provided that it is displaced so that the origin is at $\mathbf{k} = \frac{1}{64}\mathbf{b}_1 + \frac{1}{32}\mathbf{b}_2 + \frac{3}{64}\mathbf{b}_3$, and $\boldsymbol{\lambda}$ is along the (111) Cartesian direction. Such symmetry breaking is not problematic, because it becomes irrelevant when results are converged.

[13] This is even more true for very wide-gap insulators, where the electron-hole interaction is very strong. See Ref. 5.