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Calculation of linear and non-linear optical properties of amorphous Silicon

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We have used the random phase model for the electronic wave functions to calculate the imaginary part of the dielectric function $\epsilon_2(\omega)$ and the magnitude of the third harmonic generation, $|\chi^3(\omega)|$ using a model structure of a-Si containing 1728 atoms. We show that this simple calculation gives reasonable results for $\epsilon(\omega)$ and furthermore the behaviour of $\chi^3(\omega)$ is similar to more detailed theoretical calculations.

Keywords: disordered systems; semiconductors; optical properties

INTRODUCTION

The study of optical properties of solids has proved to be a powerful tool in the understanding of the electronic and atomic structure of solids. A number of techniques have been developed to calculate the linear optical properties of semiconducting materials but the situation is different for non-linear optical spectra. The non-linear response is of interest from an application point of view but also as a means of characterising surface properties. The calculation of the response function $\chi^3(\omega)$ is a time consuming business even in crystals (Moss *et al.*, 1990; Ching & Huang, 1993). The number of full band structure calculations for the third non-linear susceptibility tensor $\tilde{\chi}^{(3)}(\omega)$ is extremely small. This is because of the general complexity of the third order non-linear optical processes even for the simplest of crystals. The work of Moss *et al.* (1990) using both an empirical tight-binding and semi *ab-initio* band structure technique and that of Ching and Huang (1993) using the first principles orthogonalised linear combination of atomic orbitals method for a series of group III-IV semiconductors are the first band structure calculations of $\chi^{(3)}(\omega)$. Experimental data are very scarce, with measurements often made at only one frequency. Where experimental data exist, for example of $\chi^{(3)}(\omega)$ at zero frequency for these group III-IV crystalline semiconductors, it is gratifying that there is good agreement between these predictions and measurements.

The methods that exist for the calculation of optical properties of crystalline semiconductors especially the non-linear optical spectra exploit the periodicity of the crystal lattice. In amorphous semiconductors with no long-range order and where large structural models are required, calculations are much more difficult. Calculations or experimental measurements are almost non-existent for amorphous semiconductors.

Recently Hobbs *et al.* (1996) have devised an ingenious method solving Schrodinger's equation using the equation of motion method and calculated $\chi^3(\omega)$ for models of amorphous and crystalline Si containing 216 atoms. Their results were rather noisy probably due to the small structure of the model and they were also unable to remove the spurious divergence that occur at low frequencies although this could be corrected as described in this paper. The purpose of this

paper is to show that a simple calculation using a model structure can be used to make very reasonable estimates of $\chi^3(\omega)$.

We also make some comments on the behaviour of $\chi^3(\omega)$ at low frequencies. The work of Hobbs *et al.* (1996) was based on expressions given by Moss *et al.* (1990) and we also make use of these particular forms.

THEORY AND COMPUTATIONAL DETAILS

If the particular wave functions in a solid are written in terms of localised atomic-like orbitals

$$\psi(\vec{r}) = \sum_{nlm} a_{nlm}(j) \phi_{nlm}(\vec{r} - \vec{r}_j) \dots\dots\dots (1)$$

corresponding to orbitals labelled by nlm on a site r_j , then the random phase type of approximation assumes that the amplitudes of the orbitals can be ‘approximated’ by the form (Mott, 1967; Friedman, 1971)

$$a_{nlm}(j) = N^{-1/2} a_{nlm}^0 \exp(i\theta_{nlm}(j)) \dots\dots\dots (2)$$

where $\theta_{nlm}(j)$ is a random phase varying with the value of nlm and j , and N is the number of atoms in the solid. This assumed form cannot, of course, be true in the sense that the wave functions must satisfy Schrodinger’s equation but it does isolate terms in expressions for the response formulae that are positive definite and the hope is then that any other terms will tend to cancel out. The degree to which this is justified can be seen in calculation of say the conductivity by Okumu *et al.* (1995) in a -Si where very reasonable agreement is obtained with the computed behaviour for the conductivity as a function of energy.

The simplest way in which equation (2) may be employed is to take a_{nlm}^0 to be unity, which implies that at each energy level each orbital contributes equally to the density of states. Expressions for response coefficients then involve integrals over the electronic densities. Matrix elements of, say, the momentum operator can be evaluated for a particular structure within this approximation or the matrix elements may be treated as constants and determined empirically. We in fact will follow both routes in this work.

A refinement that was employed by Okumu *et al.* (1995) is to write

$$a_{nlm}^0 = \sqrt{\frac{g_{nlm}(E)}{\bar{g}_{nlm}(E)}} \dots\dots\dots (3)$$

where $g_{nlm}(E)$ is the partial density of states associated with the orbital labelled by nlm and $\bar{g}_{nlm}(E)$ is the average density of states over the energy range described by the localised orbitals. Yet a further refinement would be to take advantage of any knowledge of the local density of states. However for our present purpose we will simply take $a_{nlm}^0 = 1$ as this will not lead to major differences in this work.

Let us first consider the behaviour of the imaginary part of the dielectric function where (Connell, 1976)

$$\varepsilon_2(\omega) = \frac{2}{\Omega} \left(\frac{2\pi e}{m\omega} \right)^2 \sum_i \sum_f |\langle f | p | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad \dots \quad (4)$$

where Ω is the volume of the system, i and f denote the initial and final states when a photon of energy $\hbar\omega$ is absorbed, p is a component of the momentum operator. The final states must be unoccupied and the initial states occupied. If the matrix elements are treated as constants then $\varepsilon_2(\omega)$ can be written as

$$\begin{aligned} \varepsilon_2(\omega) &= 2 \left(\frac{2\pi e}{m\omega} \right)^2 \frac{a^3 \rho_{cv}^2}{\Omega} \sum_{if} \delta(E_f - E_i - \hbar\omega) \\ &\dots \quad (5) \\ &= 2 \left(\frac{2\pi e}{m\omega} \right)^2 a^3 \rho_{cv}^2 \int_0^{\hbar\omega} dE g_v(E) g_c(\hbar\omega - E) \end{aligned}$$

g_c or g_v denotes the density of states/spin/unit volume in the conduction band or valence band and is just a length of the order of the atomic spacing.

Calculations for both linear and non-linear optical spectra are performed on a model structure of silicon containing 1728 atoms (Holender & Morgan, 1991). The structure is generated using molecular dynamics starting from an amorphous model of 216 atoms and putting together a number of these blocks. This structure has about 4% over co-ordinated and 2% under co-ordinated atoms leading to gap states in the density of states shown in Figure 1 (Holender & Morgan, 1992). It is extremely difficult to generate large models without states being produced in the gap by under and over co-ordinated sites. For our present purpose we have removed the states produced by the 'defect' sites so that we create a gap of 1 eV since we are interested in interband transitions. This simple device is sufficient for our present purpose.

Moss *et al.* (1990) used perturbation theory to separate $\chi^3(\omega)$ into three contributions termed virtual electron (VE), virtual hole (VH) and three-state processes (3S). Only the VE processes will be detailed here to show the nature of the calculation. If we take matrix elements of the momentum as constants then the virtual electron contribution becomes

$$\begin{aligned} \chi_{VE}^3(\omega) &= -\frac{2}{3} \left[\frac{e}{m\omega} \right]^4 (a^3 \rho_{cv}^2)^2 \iiint \int dE_i dE_j dE_k dE_l \left[\frac{g(E_i)g(E_j)g(E_k)g(E_l)}{[E_j - E_i - 3E - 3i\xi][E_k - E_i - 2E - 2i\xi][E_l - E - E - i\xi_i]} \right. \\ &+ \frac{g(E_i)g(E_j)g(E_k)g(E_l)}{(E_j - E_i + E + i\xi)(E_k - E_i + 2E + 2i\xi)(E_l - E_i - E - i\xi)} \\ &+ \left. \frac{g(E_i)g(E_j)g(E_k)g(E_l)}{(E_j - E_i + E + i\xi)(E_k - E_i - 2E - 2i\xi)(E_l - E_i - E - i\xi)} \right] \end{aligned}$$

$$+ \frac{g(E_i)g(E_j)g(E_k)g(E_l)}{(E_j - E_i + E + i\xi)(E_k - E_i + 2E + 2i\xi)(E_l - E_i + 3E + 3i\xi)} \dots (6)$$

where E_i is in the valence band while E_j , E_k and E_l are in the conduction band. The full dielectric tensor has components of the momentum in different directions as well but we will ignore these subtleties just as we did for $\epsilon_2(\omega)$.

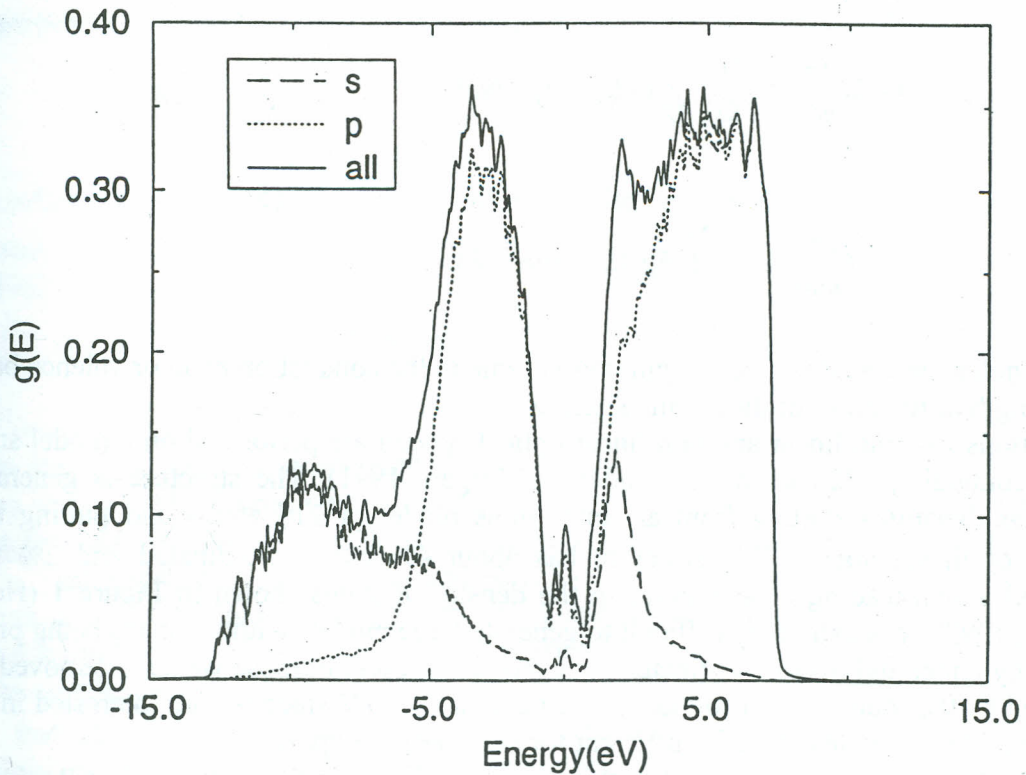


Figure 1. The electronic density of states (spin eV atom)⁻¹ for a model structure with 1728 atoms (Holender & Morgan, 1992).

An important point to consider is the behaviour of χ_3 as ω tends to zero because of the factor of ω^{-4} in the denominator. In the calculation of $\epsilon_2(\omega)$ we are assured that there is no divergence at $\omega=0$ because of the presence of the gap. If the real part of the linear response function is calculated using the Kramers-Kronig relation then a divergence in the real part is avoided by the behaviour of $\epsilon_2(\omega)$. There does not seem to be a general argument of this sort for the third harmonic generation (χ_3) in crystals based on the symmetry of the wave functions but we invoke the following argument. Inspection of (6) (and the other contributions) shows that the imaginary part of χ_3 must vanish for $E < E_g/3$ where E_g is the energy gap. The real part is given by

$$\text{Re} \chi^3 = \frac{2}{\pi} \int_0^{\infty} \frac{(\omega - \omega') \text{Im} \chi^3(\omega') d\omega'}{(\omega - \omega')^2 + \xi^2} \dots \dots \dots (7)$$

where ξ is an infinitesimal. The fact that $\text{Im} \chi^3$ does not diverge implies that $\text{Re} \chi^3$ is also well behaved. What we can expect is that $\text{Re} \chi^3$ will peak as ω sweeps through the zero in $\text{Im} \chi^3$ at $E_g/3$.

The numerical integration required some care. We used a finite value of $\xi = 1\text{eV}$ bearing in mind that the widths of the valence band are about 15eV each. This produces a spurious extension of $\text{Im} \chi^3$ below $E_g/3$. Cutting of $\text{Im} \chi^3$ with a discontinuity would produce a spurious divergence in $\text{Re} \chi^3$. We therefore smooth the sharp edge by multiplying by

$\text{Sin} \pi/2 \left(\frac{E - E_g/3}{3} \right)$ for $(E - E_g/3) \leq 1$ and unity thereafter. None of these considerations should be important as regards the general behaviour of χ^3 .

RESULTS AND DISCUSSION

In figure 2 we show the behaviour of $\epsilon_2(\omega)$ using densities of states calculated by Holender and Morgan for a model structure of a Si containing 1728 atoms (Holender & Morgan 1991). In figure 4 we show $\epsilon_2(\omega)$ fitted to the experimental results of Pierce and Spicer (1972) at an energy of 3eV and corresponds to choosing $a^3 p_{cv}^2 = 20.6au$. The peak position is around 5eV whereas the experimental results peak near 3.5eV (Figure 3). If we evaluate $\epsilon_2(\omega)$ using the simple r.p.m. then the shape will be identical to that produced by Eq. (5) but the matrix elements are now calculated using parameters for s and p-type tight binding hopping integrals of Chadi (1984). The r.p.m. yields a lower peak value than experiment and seems also to be a feature of more elaborate calculations, Weaire *et al.* (1991, 1993). Increasing the gap would push the calculated position of the peak to higher energies. This discussion of $\epsilon_2(\omega)$ is a precursor to evaluating $\chi^3(\omega)$ because we will use the value $a^3 p_{cv}^2 = 20.6au$ in those calculations.

In figures 5 and 6 we show the different contributions to $\text{Im} \chi^3$ and the total value of $|\chi|^3$. The fact that all processes seem to make comparable contributions (see figure 5) has been noted by Ching and Huang (1993). The magnitude and form of χ^3 is similar to that calculated by Hobbs *et al.* (1996) on a small structure of 216 atoms though the equation-of-motion method can lead to rather noisy results for small models and we have eliminated spurious divergences as described above.

In Fig. 6 the absolute value $|\tilde{\chi}^{(3)}(\omega)|$ is given which is to be compared with other theoretical predictions of Moss *et al.* (1990) for crystalline silicon since there are no previous calculations of $|\tilde{\chi}^{(3)}(\omega)|$ for a-Si. More recent calculations by Ching and Huang (1993) using first principles orthogonalized linear combination of atomic orbitals gave good agreement with the results of Moss *et al.* (1990). The rpm results are generally comparable with these results with the peak occurring at about 1 eV as observed in crystals. The rpm results on a-Si show a single peak as compared to the linear spectra, which was also observed in the linear spectra, which is a consequence of short-range order.

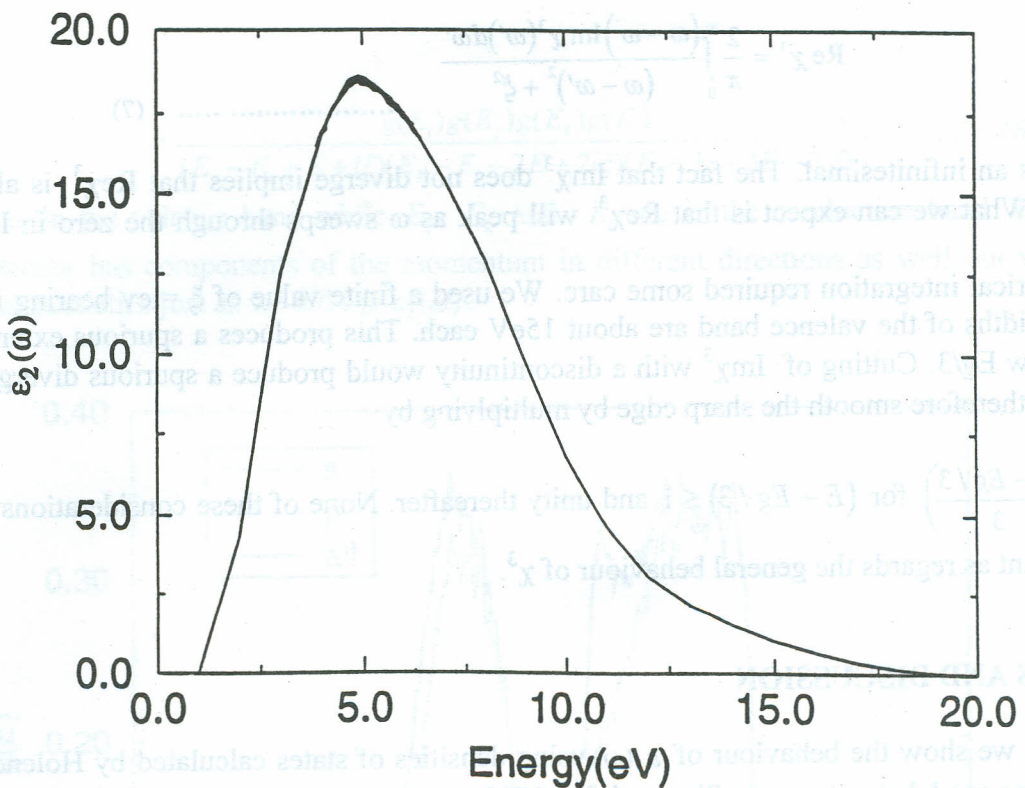


Figure 2. The imaginary part of the dielectric constant $\epsilon_2(\omega)$ in the rpm for a-Si.

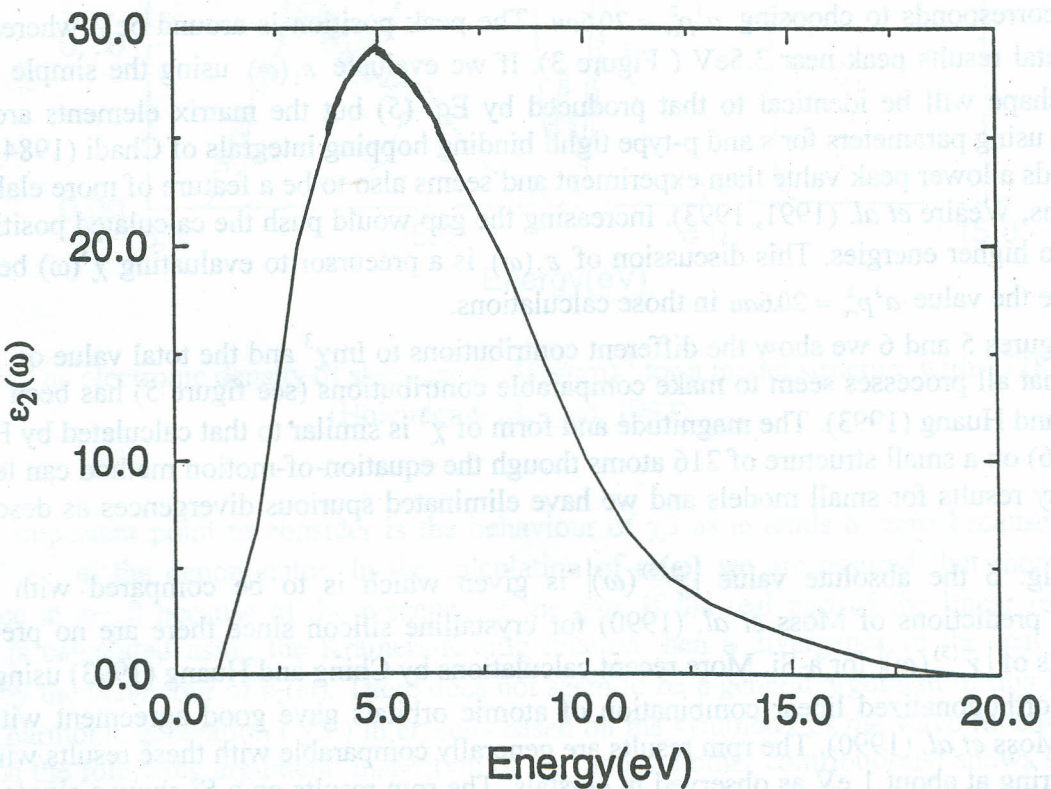


Figure 3. The imaginary part of the dielectric constant $\epsilon_2(\omega)$ calculated from Matrix elements extracted from experimental measurements for a-Si.

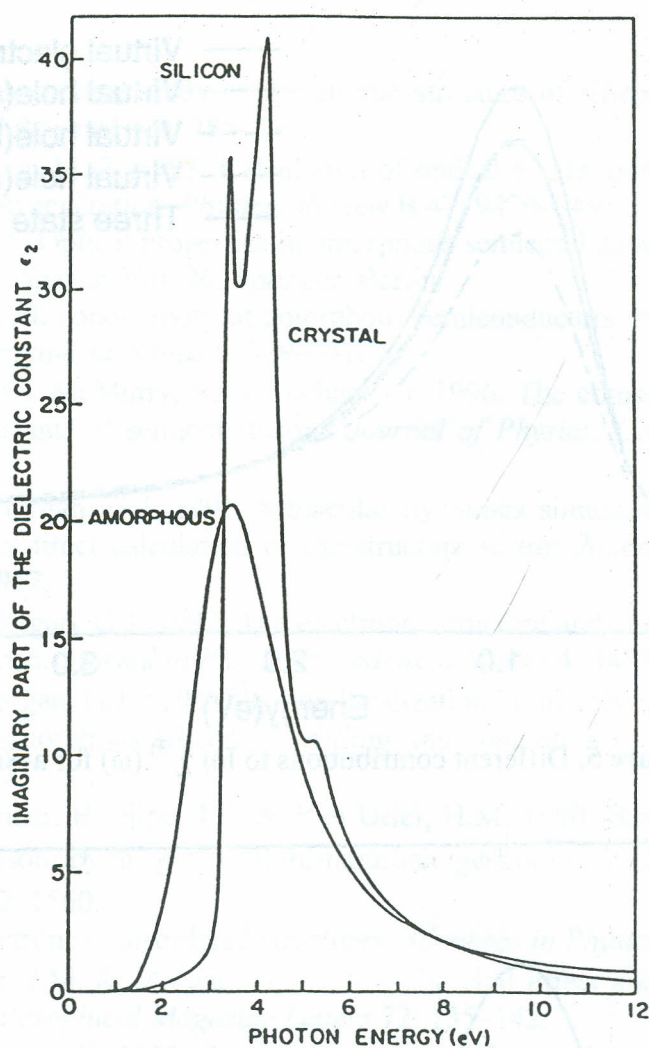


Figure 4. Experimental results of $\epsilon_2(\omega)$ for a-Si and crystalline silicon (Pierce & Spicer, 1972).

In conclusion these results demonstrate that the rpm type of approximation can be used to make good estimates of $|\tilde{\chi}^{(3)}(\omega)|$ in amorphous solids and in future it will be worthwhile extending the calculation using partial density of p and s- states which could give finer features of the spectra. These calculations also suggest that reasonable estimates of surface variation in χ^3 may also be useful making use of local density of states and evaluation of matrix elements using the tight-binding scheme.

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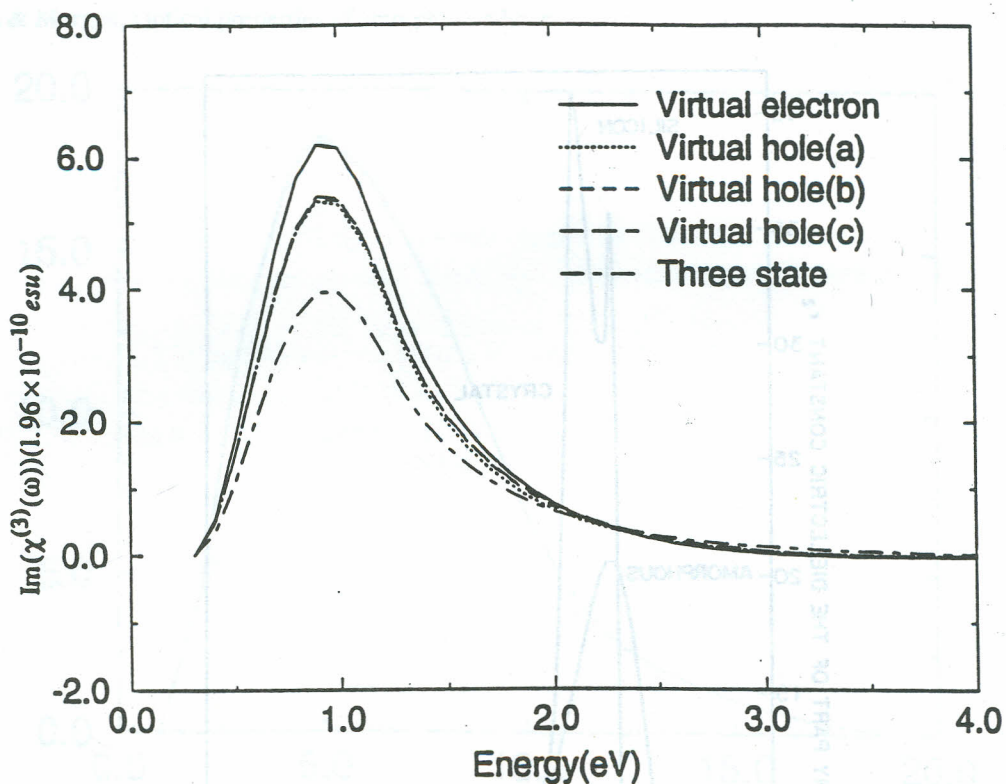


Figure 5. Different contributions to $\text{Im } \chi^{(3)}(\omega)$ for a-Si.

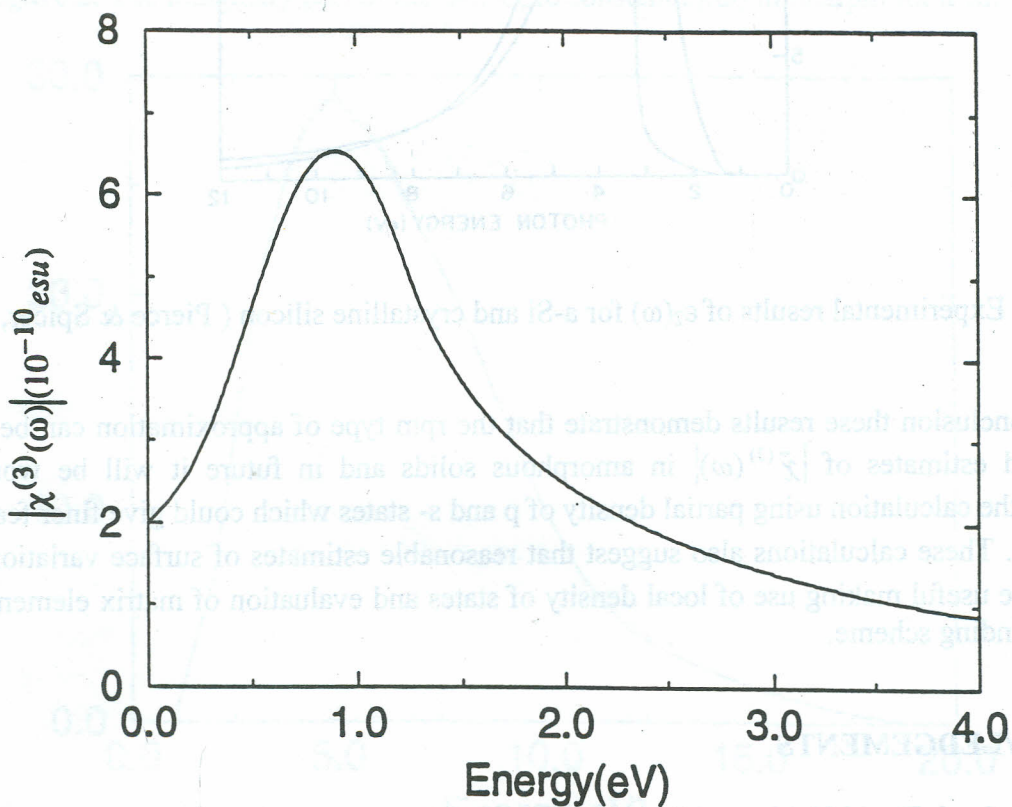


Figure 6. The absolute value of $|\chi^{(3)}(\omega)|$ for a-Si.

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