Application of the equation-of-motion method to the calculation of optical properties

LETTER TO THE EDITOR

Application of the equation-of-motion method to the calculation of optical properties

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Abstract. We show how the equation-of-motion method can be used to compute the dielectric function $\varepsilon(\omega)$ for a model of amorphous Si. The calculation uses a plane-wave basis but could be adapted to any other convenient basis. In principle, such calculations can be extended to non-linear optical properties.

The equation-of-motion method, in the sense used here, is a numerical technique originally developed to calculate electronic and vibrational densities of states of disordered solids (Alben *et al* 1975). It subsequently proved to be adaptable to the evaluation of expressions for other significant electronic properties, such as the electronic conductivity (the Kubo formula: Kramer and Weaire 1978), localization (inverse participation ratio: Weaire and Williams 1977) and spectral functions (Hickey and Morgan 1986). It is a useful alternative to the brute-force methodology of band structure integration whenever the number of eigenstates becomes so large as to render the more direct methods impracticable. Sums over eigenstates determined by matrix diagonalization are replaced by time averages of products of certain *random* vectors whose time dependence is governed by Schrödinger's equation.

In this paper we develop a further field of application of the method, in showing how it may be used for interband optical properties. Here again certain cases, particularly involving amorphous solids or non-linear coefficients, or both, can defeat the traditional methodology. For this preliminary study we take as an example the optical absorption spectrum of amorphous Si, as represented by the 216-atom structural model of Wooten and Weaire (1986). Using a pseudopotential (Hickey and Morgan 1986) we require a very large number of plane-wave basis functions: we shall use 3071 such basis functions here as has proved effective in calculations of the conductivity in a-Si (Hickey *et al* 1990a).

The standard expression for the imaginary part of the dielectric constant is (Connell 1976)

$$\varepsilon_2 = (G/\omega^2) \sum_i \sum_f |\langle f|p|i\rangle|^2 \delta(E_f - E_i - \hbar\omega) \tag{1}$$

where $G = 2\Omega^{-1} (2\pi e/m)^2$. Here ω is the frequency, i and f denote initial (valence band) and final (conduction band) wavefunctions respectively, p is a component of the momentum operator in an arbitrary direction, m and e are the mass and charge of an
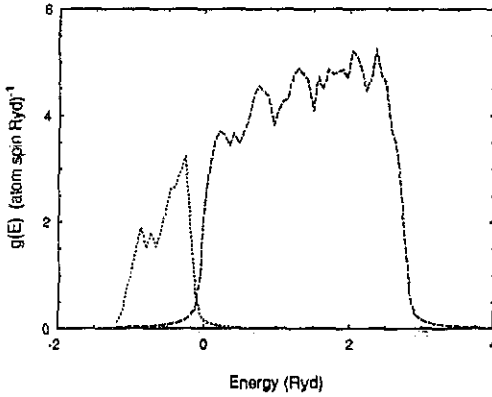
Figure 1. The densities of states for the valence band and conduction projected out of the total density. The overlap of the two bands can be reduced by increasing the run time which leads to a sharper filter function.
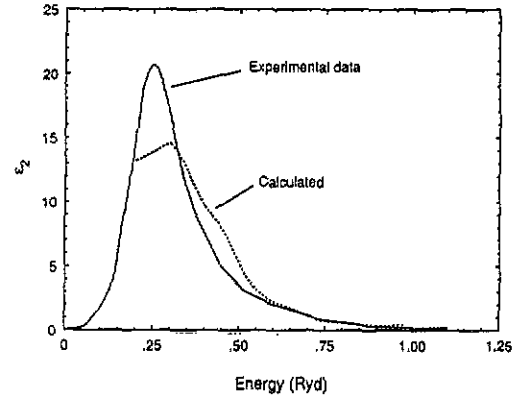

Figure 2. The behaviour of $\varepsilon_2(E)$ as a function of energy.

electron, and Ω is the volume of the system. In principle we are dealing with an isotropic system. In practice our finite model will have some slight anisotropy. Results given here are for an arbitrarily chosen direction of p. While we confine the present calculation to this familiar linear case, it should be stressed that similar techniques can be used to evaluate non-linear optical coefficients. The computational cost of the calculation of one term of the perturbation formula for a nth order optical coefficient varies only linearly with n, whereas direct evaluation will scale exponentially with n.

To compute (1) we are required to construct two normalized random vectors which represent states $|v\rangle$ and $|c\rangle$ confined to the subspaces of the valence and conduction bands respectively. This may be done by projecting out such parts from a completely random initial choice, as described by Hickey *et al* (1990a, b). Figure 1 shows the partial densities of states of the two bands, as given by the equation-of-motion method, using two such vectors normalized to N_v and N_c respectively, the number of eigenstates in the two bands. $N_v = 2N$, where N is the number of atoms in the finite sample of a-Si. It is perfectly possible to project out the valence and conduction bands more precisely using longer run times but this is not important in the context of the present paper where the emphasis is on the usefulness of the equation-of-motion method. In general, this projection method is a very useful procedure because it could be used to perform self-consistent calculations and to study very large models by projecting out a narrow range of eigenstates and thereby reducing the time step in the equation-of-motion method.

As in other developments of the method, the Schrödinger equation is integrated to obtain the time-dependent vectors $|v(t)\rangle$ and $|c(t)\rangle$. Using these, the expression (1) may be evaluated for $E = \hbar\omega$ as

$$\varepsilon_2 = \pi^{-1} G E^{-2} \hbar^2 \text{Im}\left[\lim_{T\to\infty} T^{-1} \frac{\text{i}}{\hbar} \int_0^T \text{d}t\, \langle v(t)|p|c(t)\rangle\, e^{(\text{i}/\hbar)(E-\text{i}\eta)t}\right.$$

$$\left. \times \int_t^\infty \text{d}t'\, e^{-(\text{i}/\hbar)(E-\text{i}\eta)t'} \langle c(t')|p|v(t')\rangle\right] \tag{2}$$

and η is a damping parameter. Use of finite η implies Lorentzian broadening of the final result, that is, convolution with the function $f(E) = \pi^{-1}\eta(E^2 + \eta^2)^{-1}$.

To show this, expand the two time-dependent vectors as sums over eigenstates $|n\rangle$ and $|m\rangle$ belonging to the relevant bands:

$$|v(t)\rangle = \sum_n a_n \, e^{-iE_n t/\hbar} |n\rangle \tag{3}$$

$$|c(t)\rangle = \sum_m b_m \, e^{-iE_m t/\hbar} |m\rangle. \tag{4}$$

Most of the resulting products are associated with complex exponentials which average to zero as $T \to \infty$ in (2). The expression in square brackets thus reduces to

$$\sum_m \sum_n \frac{|a_n|^2 |b_m|^2 |\langle n|p|m\rangle|^2}{E_m - E_n - E - i\eta}. \tag{5}$$

The quantities $|a_n|^2$ and $|b_n|^2$ are random variables and we normalize the wavefunction so that their average value is unity. This completes the proof of the equivalence of (1) and (2), apart from the fluctuations due to these random variables, which are largely suppressed by the broadening of the spectrum entailed by the introduction of finite η.

As a consequence of the finite resolution associated with η and the projection into the two subspaces, such a method will not yield a zero value of ε_2 for energies less than the band gap. Indeed, the result diverges as E^{-2} as $E \to 0$, due to the prefactor in (2). Fluctuations due to the small size of the sample are then more pronounced at large E. It is, therefore, not useful for this small model in relation to the details of optical absorption edges, but can give information on the broad features of interband absorption at higher energies. In the present case, there is a single peak at approximately $E = 0.25$ Ryd (Pierce and Spicer 1972), which is well reproduced by the calculation (figure 2). Other less-pronounced features are artefacts of the finite structural model used, and can be further reduced by calculations for larger models. Much larger models and run times can be handled using tight-binding schemes to describe the electronic structure. The fact that the height of the calculated peak is smaller than the experimental value is easily explained by the smoothing effect of the finite value of η. The calculations reported here correspond to using a time step τ which is one-tenth of $2\pi\hbar/E_{\max}$ where $E_{\max}$ is the total band width (3.7 Ryd). The value of η chosen is $\eta = 0.05$ Ryd which convolutes the results with a Lorentzian of half-width 0.05 Ryd, and this relatively large value is necessary to suppress unphysical 'noise' due to the finite size of the system. In conclusion, this calculation would appear to confirm the validity of the equation-of-motion method for the calculation of interband optical properties, and encourage its further development towards non-linear coefficients in particular.

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