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# Optical lineshapes of impurities in crystals: a lattice model of inhomogeneous broadening by point defects

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**Abstract.** Previous theories of inhomogeneous broadening by point defects of impurity transitions in crystals have invoked a continuum approximation for the defect positions. We generalize these theories by treating the crystal as a discrete lattice. At low defect densities we recover the results of the continuum theory, finding a Lorentzian lineshape. At high defect densities the lineshape is approximately Gaussian. At intermediate densities, the lineshape displays satellite structure due to different configurations of nearby defects. For all densities we derive approximate analytic expressions for the lineshape that are in good agreement with exact numerical results.

## 1. Introduction

When dilute impurities are present in a host crystal lattice, at low temperatures the absorption zero-phonon line of a distinct impurity transition has a breadth that is due to the local disorder in the vicinity of each impurity. That is, physical or chemical imperfections in the crystal produce a unique microscopic environment around each impurity, causing a shift of its transition frequency. The superposition of many sharp lines with different frequencies (from the many impurities) leads to a smooth lineshape usually much broader than that due to a single impurity. This situation is called inhomogeneous broadening. The inhomogeneous impurity lineshape can provide a useful probe of disorder in crystals, which plays an important role in determining electronic and structural properties. Specifically, with a microscopic theory one would hope to be able to determine from the experimental lineshape the concentration and nature of the crystal defects.

A comprehensive review of the theory of inhomogeneous broadening in crystals was provided over two decades ago by Stoneham [1]. One of the main assumptions of the theory is that the defects responsible for line broadening are uncorrelated with each other, which restricts the validity of the theory to low defect densities, in which case it is useful to treat the lattice as a continuum. Within this picture Stoneham finds that dislocations lead to lineshapes that are nearly Gaussian, while point electric dipole or strain defects produce a Lorentzian lineshape. These general features have been verified experimentally [2, 3].

Subsequently Davies [4] focused on the case of point defects within the continuum approximation, and found that if defects are excluded from a spherical region of radius  $R$  around the impurity, in the limit  $\rho R^3 \gg 1$  ( $\rho$  is the defect density) the lineshape becomes Gaussian. Much the same conclusion was arrived at somewhat later but apparently independently by Kador [5]. One could realize the above inequality by keeping  $R$  fixed

and letting  $\rho$  become large, but this is in contradiction with the assumption of low defect density implicit in these theories. Alternatively one could consider a fixed (and small)  $\rho$ , and let  $R$  become large. Here, however, it is not clear physically why defects should be excluded from within a large sphere around an impurity. Therefore it seems to us that there are some problems in deriving a Gaussian lineshape within the continuum theory.

In addition, whereas in many crystals defect densities really are quite low, in several highly disordered crystals such as benzoic acid and p-terphenyl (which have attracted some recent attention [6–12] as possible well defined model systems for truly amorphous solids) and in mixed crystals, defect densities can be much higher. In order to understand spectroscopic experiments on these systems, especially the appearance and shape of satellite bands [13, 14], one must go beyond the continuum approximation.

For the above reasons we decided to generalize the traditional low-density continuum theory of inhomogeneous broadening by point defects to a lattice model that is capable of describing systems with high defect densities. In section 2 we introduce the theoretical model, derive a general expression for the lineshape that is amenable to numerical evaluation, and calculate analytic results valid at low and high defect densities, finding Lorentzian and Gaussian lineshapes respectively. We also present useful approximations to the lineshape at intermediate defect densities, when satellite bands due to nearby defects are present. In section 3 we compare our approximate results to exact numerical calculations, and in section 4 we conclude with a few remarks.

## 2. Lattice model of inhomogeneous lineshapes

In our theoretical model we consider a single impurity chromophore residing at a specific substitutional or interstitial site of the host crystal, which we will take to be the origin. We also imagine that point defects, which could include chemical or isotopic impurities or vacancies, can reside at a well defined set of substitutional or interstitial sites. This set of sites accessible to defects will be labelled by the index  $i$ , and will be called the defect lattice. For simplicity we will assume that there is only one kind of defect, although the theory could easily be generalized to relax this restriction. Each site  $i$  will then be described by a discrete occupation variable  $\xi_i$ , which can take on the values 0 or 1, corresponding respectively to the absence or presence of a defect. For simplicity we will assume that at each site  $i$  the probability of being occupied by a defect is  $p$ , which is independent of the occupancy of the other sites. Thus if we denote the set of occupation variables by the vector  $\xi = (\xi_1, \xi_2, \dots)$ , and the probability of obtaining a defect configuration  $\xi$  by  $\mathcal{P}(\xi)$ , then

$$\mathcal{P}(\xi) = \prod_i P(\xi_i) \quad (1)$$

and

$$P(\xi) = p\delta_{\xi 1} + (1 - p)\delta_{\xi 0}. \quad (2)$$

This probability distribution is clearly normalized such that

$$\sum_{\xi} \mathcal{P}(\xi) = 1. \quad (3)$$

Thus we see that in our model the defects are uncorrelated except that each site of the defect lattice can be occupied by at most one defect. Our assumption that each defect site is

described by an independent occupation variable may not always be a good approximation, in which case a more elaborate theory involving clustering effects could presumably be worked out.

We next assume that the presence of a single defect at site  $i$  shifts the transition frequency of the chromophore by an amount  $v(r_i)$ , which, as indicated, depends on the position of the defect,  $r_i$ . We further assume that the total perturbation of the chromophore's transition frequency is simply the sum of the shifts from the individual defects [1]. Therefore, for a particular defect configuration  $\xi$ , the transition frequency is

$$\omega(\xi) = \omega_0 + \sum_i \xi_i v(r_i) \quad (4)$$

where  $\omega_0$  is the transition frequency for the chromophore in a crystal with no defects.

If we now neglect the phonon side band of the chromophore transition and any homogeneous broadening of the zero-phonon line [15-17], then for each configuration the lineshape is simply a delta function, and the observed inhomogeneous lineshape is the configurational average

$$I(\omega) = \langle \delta(\omega - \omega(\xi)) \rangle \quad (5)$$

where

$$\langle F(\xi) \rangle \equiv \sum_{\xi} \mathcal{P}(\xi) F(\xi). \quad (6)$$

We note that at low temperatures homogeneous linewidths are usually completely overwhelmed by inhomogeneous broadening and so the above formulation is reasonable. At higher temperatures, when homogeneous broadening cannot be neglected, its effect can be included by an appropriate convolution with the inhomogeneous lineshape.

To facilitate the configurational average we can write the delta function in its spectral representation, and then the lineshape becomes a Fourier transform of the 'generating function'  $G(t)$ :

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{it(\omega - \omega_0)} G(t) \quad (7)$$

where

$$G(t) \equiv \langle e^{-it \sum_i \xi_i v(r_i)} \rangle. \quad (8)$$

Writing the exponential of the sum as the product of exponentials allows us to perform the configurational average to obtain

$$G(t) = \prod_i \{1 + p(e^{-itv(r_i)} - 1)\}. \quad (9)$$

This can be further rearranged to give

$$G(t) = \exp \left\{ \sum_i \ln[1 + p(e^{-itv(r_i)} - 1)] \right\} \quad (10)$$

which, together with equation (7), provides a useful expression for either exact numerical or approximate analytical evaluation.

First let us consider the limit of low defect density, when  $p \ll 1$ . In this case the logarithm can be expanded to obtain

$$G(t) = \exp \left\{ p \sum_i (e^{-iv(r_i)} - 1) \right\}. \quad (11)$$

It will also be useful to expand equation (10) in powers of  $v(\mathbf{r})$  to obtain

$$G(t) = \exp \left\{ \sum_{n=1}^{\infty} \frac{(-it)^n}{n!} g_n(p) M_n \right\} \quad (12)$$

where

$$M_n = \sum_i v(r_i)^n \quad (13)$$

and the first few  $g_n(p)$  are given by

$$\begin{aligned} g_1(p) &= p & g_2(p) &= p - p^2 & g_3(p) &= p - 3p^2 + 2p^3 \\ g_4(p) &= p - 7p^2 + 12p^3 - 6p^4. \end{aligned} \quad (14)$$

If the inequalities

$$|g_4(p) M_4 / 6g_2(p)^2 M_2^2| \ll 1 \quad (15)$$

and

$$|\sqrt{2}g_3(p) M_3 / 3(g_2(p) M_2)^{3/2}| \ll 1 \quad (16)$$

are satisfied, then it is permissible to truncate equation (12) at second order, which leads to a Gaussian expression for the lineshape:

$$I(\omega) = (1/\sqrt{2\pi\sigma^2}) e^{-(\omega - \tilde{\omega})^2 / 2\sigma^2} \quad (17)$$

where

$$\tilde{\omega} = \omega_0 + pM_1 \quad (18)$$

and

$$\sigma^2 = (p - p^2)M_2. \quad (19)$$

Now let us specialize to the case of dipolar chromophore-defect interactions. Supposing first that these interactions have an electrostatic origin, if we assume that the difference between the permanent electric dipole moments of the excited and ground state chromophore is  $p_c$ , and that the presence of a defect changes the electric dipole moment of the defect site by an amount  $p_d$ , then the frequency shift due to a single defect at position  $r$  is

$$v(r) = p_c p_d [\hat{p}_c \cdot \hat{p}_d - 3(\hat{p}_c \cdot \hat{r})(\hat{p}_d \cdot \hat{r})] / \hbar r^3 \quad (20)$$

where  $\hat{p}_c = p_c/p_c$ ,  $p_c$  is the magnitude of  $p_c$ , and similarly for  $\hat{p}_d$  and  $p_d$ . This can be rewritten as

$$v(r) = \Lambda \Psi(\Omega)(a/r)^3 \quad (21)$$

where  $\Lambda = p_c p_d / \hbar a^3$  has units of frequency,  $\Psi$  is a dimensionless function of the angles  $\Omega = (\theta, \phi)$ , and  $a^3$  is the volume per lattice site of the defect lattice. One finds, conveniently, that the frequency shift from elastic strain interactions with point defects has a form identical to equation (21) [1, 4].

In the low-density limit one can obtain an approximate expression for the lineshape by converting the sum in equation (11) to the integral

$$\ln G(t) = \frac{P}{a^3} \int_R^{R_2} r^2 dr \int d\Omega (e^{-it\Lambda\Psi(\Omega)a^3/r^3} - 1) \quad (22)$$

and then taking the limits  $R \rightarrow 0$  and  $R_2 \rightarrow \infty$ . In fact, at this point our theory becomes identical to Stoneham's; using the fact that

$$\int d\Omega \Psi(\Omega) = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \Psi(\theta, \phi) = 0 \quad (23)$$

which follows from the definition of  $\Psi(\Omega)$  in equation (21), he evaluates this integral in his appendix III to obtain [1]

$$G(t) = e^{-i\Delta\omega t - \Gamma|t|} \quad (24)$$

with

$$\Delta\omega = -\frac{p\Lambda}{3} \int d\Omega \Psi(\Omega) \ln|\Psi(\Omega)| \quad (25)$$

$$\Gamma = \frac{\pi p\Lambda}{6} \int d\Omega |\Psi(\Omega)|. \quad (26)$$

This then produces the Lorentzian lineshape

$$I(\omega) = (\Gamma/\pi)/[(\omega - \tilde{\omega})^2 + \Gamma^2] \quad (27)$$

with

$$\tilde{\omega} = \omega_0 + \Delta\omega. \quad (28)$$

In order to ascertain when one might obtain the Gaussian lineshape of equation (17), we can estimate the magnitudes of  $M_2$ ,  $M_3$ , and  $M_4$  in the inequalities (15) and (16) by again converting sums to integrals, this time in equation (13), to get

$$M_n = \frac{1}{a^3} \int_R^{R_2} r^2 dr \int d\Omega \Lambda^n \Psi(\Omega)^n \left(\frac{a}{r}\right)^{3n}. \quad (29)$$

Using equation (23) we see that  $M_1 = 0$ , and for the higher values of  $n$  one can smoothly take the limit  $R_2 \rightarrow \infty$  to obtain

$$M_n = [4\pi \Lambda^n / 3(n-1)] (a/R)^{3(n-1)} \langle \Psi^n \rangle \quad n \geq 2 \quad (30)$$

where

$$\langle \Psi^n \rangle = \frac{1}{4\pi} \int d\Omega \Psi(\Omega)^n. \quad (31)$$

Assuming for a moment that the chromophore occupies a single site of the defect lattice, which is thereby inaccessible to defects, it is reasonable to determine the lower cutoff  $R$  by setting  $a^3 = 4\pi R^3/3$ . In this case the inequalities (15) and (16) necessary for a Gaussian lineshape become

$$|g_4(p)\langle \Psi^4 \rangle / 18g_2(p)^2 \langle \Psi^2 \rangle^2| \ll 1 \quad (32)$$

and

$$|g_3(p)\langle \Psi^3 \rangle / 3\sqrt{2}(g_2(p)\langle \Psi^2 \rangle)^{3/2}| \ll 1. \quad (33)$$

For small  $p$ , since  $g_n(p) \simeq p$ , these inequalities will not be satisfied (indeed, we have just seen above that the lineshape is approximately Lorentzian in this limit). The largest  $p$  that is necessary to consider is  $p = \frac{1}{2}$ , since for any larger defect densities one would simply redefine the problem so that the reference crystal has all defect sites occupied by defects. For this value of  $p$  the left hand side of equation (33) is identically 0, and equation (32) becomes

$$\langle \Psi^4 \rangle / 9 \langle \Psi^2 \rangle^2 \ll 1 \quad (34)$$

which suggests that the lineshape will in fact be approximately Gaussian for  $p = \frac{1}{2}$ .

Next let us recall that Davies [4] considered the case of dipolar interactions within the continuum model, and that defects were excluded from a large sphere of radius  $R$  around the chromophore. We can discuss this case within our lattice model by taking  $p \ll 1$  (which is when the continuum model is valid) and  $R \gg a$ . When the latter condition is satisfied, equation (30) for  $M_n$  becomes an excellent approximation, and, ignoring numerical factors, the inequalities of equations (15) and (16) yield simply  $\rho R^3 \gg 1$  (where  $\rho = p/a^3$  is the defect density). Thus in this limit the lineshape is Gaussian, and is given by equation (17), where  $\tilde{\omega} = \omega_0$ , and

$$\sigma^2 = \frac{p\Lambda^2 a^3}{3R^3} \int d\Omega \Psi(\Omega)^2 \quad (35)$$

which is in agreement with Davies [4].

Although the idea of excluding defects from within a sphere around the chromophore is not particularly physically reasonable in our minds, the fact that in this case the lineshape tends to a Gaussian does suggest an approximate scheme for calculating the lineshape when *no* defects are excluded, which will be important for intermediate  $p$ , when this lineshape is neither Gaussian nor Lorentzian. The basic idea is to treat the nearby and hence strongly interacting defects exactly, while treating the defects farther away in an approximate manner. A similar scheme was also suggested by Stoneham [1] and by Jaaniso *et al* [14]. To this end, let us assume that the defects on lattice sites  $i = 1, 2, \dots, S$  are to be treated exactly. To do so, we begin with equation (5), and explicitly perform the configurational average over the occupation variables  $\xi_1, \xi_2, \dots, \xi_S$ . The result can be written as

$$I(\omega) = \sum_{j=1}^{2^S} w_j \left\langle \delta(\omega - \omega_0 - \omega_j - \sum_i \xi_i v(r_i)) \right\rangle \quad (36)$$

where the  $S$  special sites are excluded in  $\sum'_i$ . As seen, there are  $2^S$  terms in the sum, each corresponding to a distinct defect configuration  $j$  (for the  $S$  sites), which is specified by a particular realization of the occupation variables, labelled  $\xi_1^j, \xi_2^j, \dots, \xi_S^j$ . The weight factors  $w_j$  are of the form

$$w_j = p^{m_j} (1 - p)^{S - m_j} \quad (37)$$

where

$$m_j = \sum_{i=1}^S \xi_i^j \quad (38)$$

which is simply the number of occupied sites in configuration  $j$ , and the frequency shifts are given by

$$\omega_j = \sum_{i=1}^S \xi_i^j v(r_i). \quad (39)$$

At this point we can proceed as before, obtaining

$$I(\omega) = \sum_{j=1}^{2^S} \frac{w_j}{2\pi} \int_{-\infty}^{\infty} dt e^{it(\omega - \omega_0 - \omega_j)} G'(t) \quad (40)$$

where

$$G'(t) = \langle e^{-it \sum'_i \xi_i v(r_i)} \rangle. \quad (41)$$

If the generating function  $G'(t)$  leads to a lineshape  $I'(\omega)$ , where

$$I'(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{it(\omega - \omega_0)} G'(t) \quad (42)$$

then the full lineshape can be written simply as

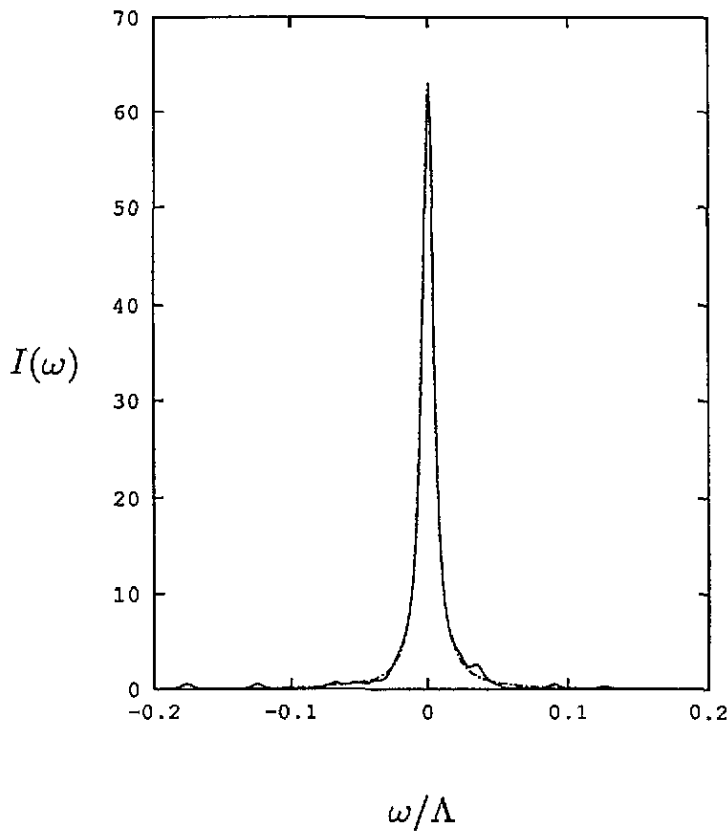
$$I(\omega) = \sum_{j=1}^{2^S} w_j I'(\omega - \omega_j). \quad (43)$$

This kind of analysis is especially useful if enough sites have been treated exactly so that the residual lineshape  $I'(\omega)$  is approximately Gaussian. This will be the case if the inequalities of equations (15) and (16), with  $M_n$  replaced by their 'primed' counterparts

$$M'_n = \sum'_i v(r_i)^n \quad (44)$$

are satisfied. If they are, then the lineshape  $I'(\omega)$  is given by equation (17), but with  $M_1$  and  $M_2$  replaced by  $M'_1$  and  $M'_2$ .





**Figure 1.** Absorption lineshape for  $p = 0.001$ . The exact result is given by the full curve. The Lorentzian approximation is given by the chain curve.

### 3. Results

In order to obtain numerical results with which to compare our analytic approximations, we consider a simple cubic defect lattice whose origin is occupied by the chromophore, and for simplicity we assume that the dipolar chromophore–defect interaction is electrostatic and that all permanent dipoles are in the  $\hat{z}$  direction so that

$$\Psi(\theta, \phi) = 1 - 3 \cos^2 \theta. \quad (45)$$

With this model, the Fourier transform in equation (7), with equation (10) for  $G(t)$ , was performed numerically. For this calculation we of course considered a finite number of sites. From equation (5) we know that in this case the exact lineshape is actually a sum of (very closely spaced) delta functions. In the time domain this means that the generating function  $G(t)$  decays approximately to zero, but then has recurrences, albeit at very long times. Therefore, in order to perform the transform numerically, we added a convergence factor with a very small amount of exponential damping. The damping rate was decreased and the number of sites was increased until the results were independent of both.

We present results for  $p = 0.001$  in figure 1, where we plot the numerically exact lineshape versus the dimensionless frequency  $\omega/\Lambda$ , and we set the reference frequency  $\omega_0$

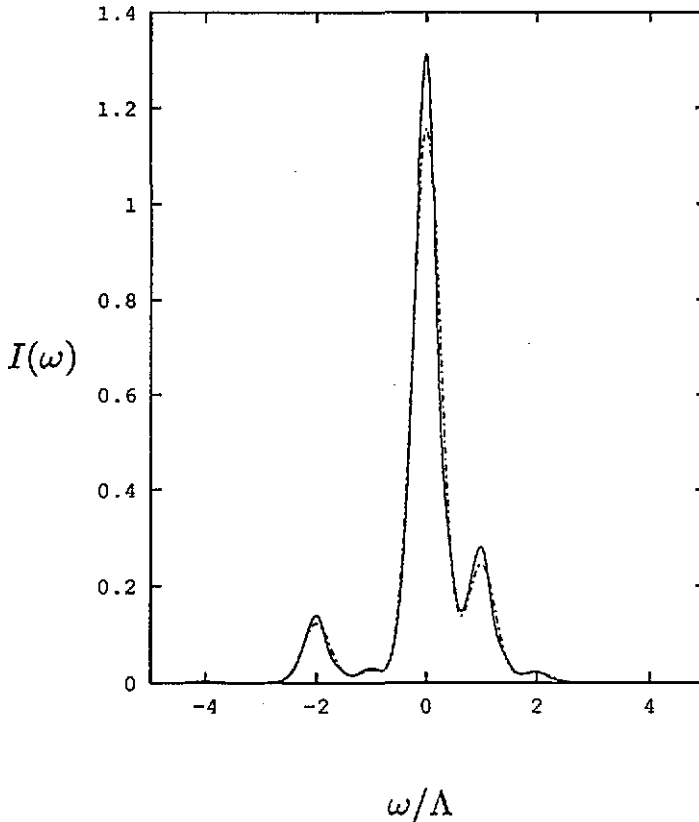


Figure 2. Absorption lineshape for  $p = 0.05$ . The exact result is given by the full curve. The chain curve represents an exact treatment of the six nearest-neighbour defect sites, with the Gaussian approximation for the rest of the crystal.

to zero. The weak structure in the wings of the line is real, and not due to numerical noise. In comparison, we have also plotted the Lorentzian approximation from equation (27), which should be valid in this low-density case. We see that although this approximation does not give the weak structure correctly (as a result of converting the sum in equation (11) to an integral) it does provide a good approximation to the central peak.

Figure 2 presents the results for  $p = 0.05$ . The exact result shows significant satellite structure, which is due to different configurations of the nearest defects. The form of the lineshape suggests that a reasonable approximation might be to treat the six sites that are nearest neighbours of the chromophore exactly, and then use the Gaussian approximation for the remaining defects, as discussed at the end of the last section. To this end, we have evaluated the left hand side of the inequalities (15) and (16) for  $p = 0.05$ , with equation (44) for  $M'_n$ . This gives 0.11 and 0.12 respectively, which indicates that this approach may be useful. Thus the approximation from equation (43), with equations (17)–(19) and (44), is also shown in figure 2, which gives reasonable but not quantitative agreement with the exact result. To obtain quantitative agreement one would have to treat more defect sites exactly.

In figure 3 we show results for  $p = 0.25$ . The exact lineshape shows structure in the

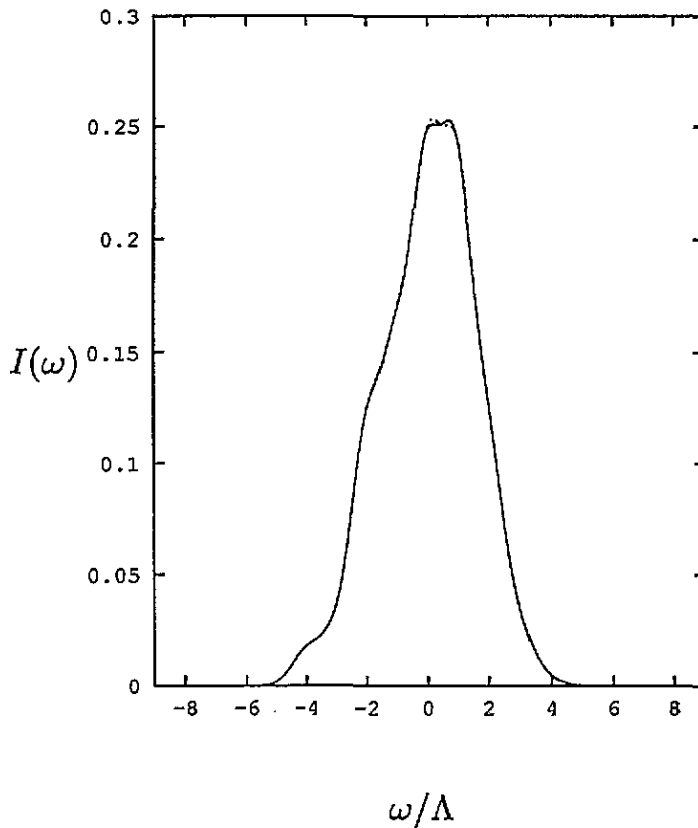


Figure 3. Absorption lineshape for  $p = 0.25$ . The exact result is given by the full curve. The chain curve represents an exact treatment of the six nearest-neighbour defect sites, with the Gaussian approximation for the rest of the crystal. As shown, it is indistinguishable from the exact result, except near the maximum.

form of shoulders on a central peak. This larger value of  $p$  strengthens the inequalities of equations (15) and (16), and so treating the six nearest neighbours exactly with the Gaussian approximation for the rest of the sites should work better than it did for  $p = 0.05$ . This result is also shown in figure 3, giving excellent agreement with the exact result.

Figure 4 shows the results for  $p = 0.5$ , the highest possible value for  $p$ . The exact result shows a single broad feature. As suggested by the approximate argument leading to equation (34), and confirmed by an exact evaluation of the left hand side of the inequalities (15) and (16), the Gaussian approximation of equation (17) (without treating any sites exactly) should be reasonably good. This calculation is also shown in figure 4, giving pretty good agreement with the exact result. To improve upon this result we can truncate the expansion of equation (12) at fourth order, and perform the Fourier transform numerically. As shown in figure 4 this approach produces a very accurate lineshape. Alternatively, one can treat the nearest neighbours exactly, as discussed above, which leads to a lineshape indistinguishable from the exact result, and is not shown.

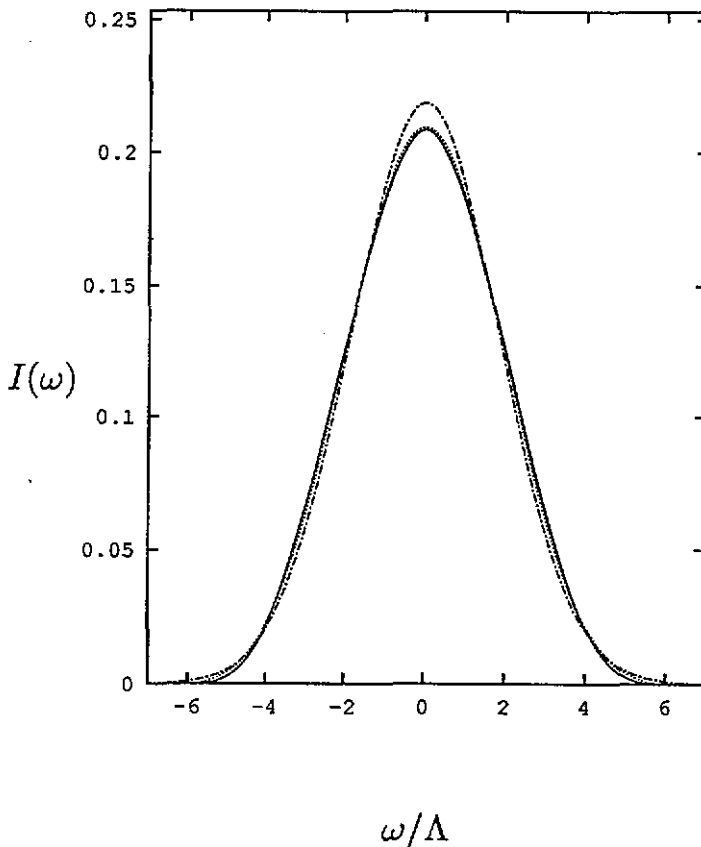


Figure 4. Absorption lineshape for  $p = 0.50$ . The exact result is given by the full curve. The chain curve represents the Gaussian approximation with no defect sites treated exactly. The dotted curve follows from the fourth-order truncation of equation (12), and numerical Fourier transformation.

#### 4. Concluding remarks

In summary, we have considered a lattice model of inhomogeneous broadening by point defects that is valid for any defect density. In the limit of low defect density, we recover the continuum theory of Stoneham [1], finding a lineshape that is approximately Lorentzian. When the defect density is not low, the lineshape shows significant structure due to the configurations of nearest-neighbour sites. At the largest defect density, where half the sites are occupied by defects, the lineshape becomes approximately Gaussian. We have developed several approximation schemes that provide accurate lineshapes for all densities, as verified by comparison with exact numerical calculations.

For numerical computation we assumed that possible defect sites formed a simple cubic lattice, and that the defect-chromophore interaction was given simply by the  $zz$  component of the dipole tensor. More complicated and realistic lattices and interactions could certainly be studied—we do not expect any qualitatively different results. It would also be interesting to consider the case of defect-defect or defect-chromophore correlation (apart from the multiple occupancy exclusion treated herein), e.g. clustering. Experimental results that might benefit from a theoretical analysis of the sort described in this paper have been

obtained [13, 14] for the mixed crystal systems  $\text{LaCl}_{3-x}\text{Br}_x:\text{Nd}^{3+}$  and  $\text{SrFBr}_{1-x}\text{Cl}_x:\text{Sm}^{2+}$ . Indeed, the evolution of the absorption spectra in figures 1–4 (as the defect concentration is increased) qualitatively describes that observed experimentally [14].

In the case of chromophore spectroscopy in glasses, it is clear that some interesting non-linear line-narrowing and hole-burning experiments probe the correlation of the inhomogeneous frequency distributions for two different transitions on the same chromophore [18, 19]. It will be interesting to calculate this correlation for crystalline hosts. Within the continuum model some work on this problem has already appeared [20]. The correlation of transition frequencies on *different* chromophores is of great interest in the context of energy transfer and localization, and we will be generalizing our previous work [21] on glasses to the present lattice model of crystals.

Finally, some fascinating fluorescence excitation spectroscopy experiments on single chromophores in disordered crystals have shown evidence of spectral diffusion—the transition frequency of individual molecules jumps around in time [10, 11]. It has been suggested that this dynamics results from rearrangements of the local environment around each chromophore. If this local environment is due to point defects, then a dynamic generalization of the lattice model considered herein may describe some aspects of these experiments. We are currently pursuing this idea.

## Acknowledgments

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