

A statistical topographic model for exciton luminescence spectra

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Abstract. Some features of the absorption and luminescence spectra of excitons in disordered 2D semiconductors appear to be nearly universal over a wide range of samples. In particular, the offset of the peaks of these two spectra is proportional to their linewidths, over a range of two orders of magnitude. We show that the relationship between these spectra can be understood in terms of the statistical properties of a Gaussian random function: the absorption spectrum is proportional to the probability distribution of the function itself, whereas the luminescence spectrum is proportional to the distribution of the heights of the minima of the function.

1. Introduction

Figure 1(a) shows the absorption (solid curve) and luminescence (dashed curve) spectra of a semiconductor system. The absorption spectrum includes a large peak due to direct creation of excitons (hydrogenically bound electron-hole pairs). The luminescence peak is due to the recombination of the exciton pairs. The sample is a multiple-quantum-well system, in which the excitons are confined to one of a number of two-dimensional layers sandwiched between regions of a higher bandgap. Figure 1(b) is another spectrum for a similar system, this time produced from different materials. The similarity between the lineshapes and relative offsets of the spectra in these two pictures is quite marked. Figure 2 summarizes information from many such experiments: the offset of the peak of the luminescence curve from that of the absorption curve is found to be proportional to the full width at half maximum of the absorption peak, over a range of nearly two orders of magnitude. The figure contains data from many different samples containing excitons confined to two dimensions (different mixtures of semiconductors, layer widths, and different growth techniques). This paper will show that the striking near universality of the relative shift of the two spectra is explained by a very simple model involving the geometry of a Gaussian random function.

We describe a simple geometrical model for the physical origin of the absorption and luminescence spectra in section 2. Our model implies that the absorption spectrum is proportional to the probability distribution of a random function $E(x, y)$ (which represents the energy of a stationary exciton at position (x, y)). After the excitons are created, they lose energy rapidly by exciting phonons, and become trapped in minima of $E(x, y)$ (see figure 3). The luminescence spectrum is therefore

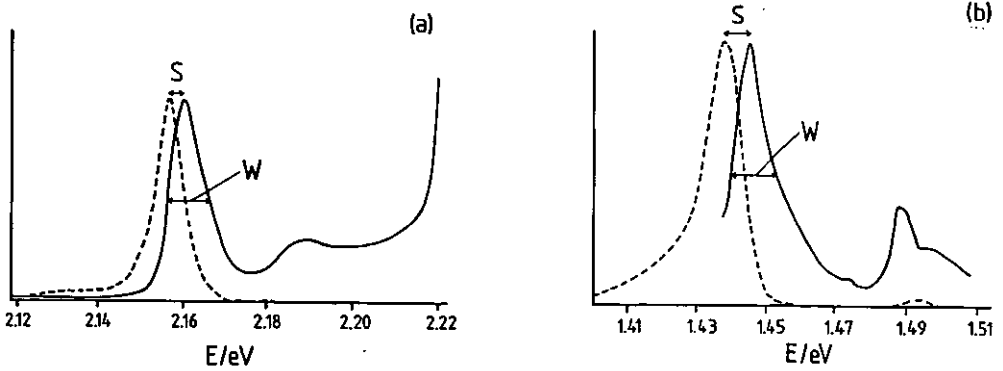


Figure 1. Absorption spectrum (solid curve) and luminescence spectrum (dashed curve) of two multiple-quantum-well semiconductor systems. The curves look very similar, despite the fact that the materials are different. The two arrows indicate the offset S of the two peaks, and the full width at half-maximum W of the absorption line. The figures are redrawn from (a) Stanley (1991), CdZnTe/ZnTe, and (b) Brandt *et al* (1992), InAs/GaAs.

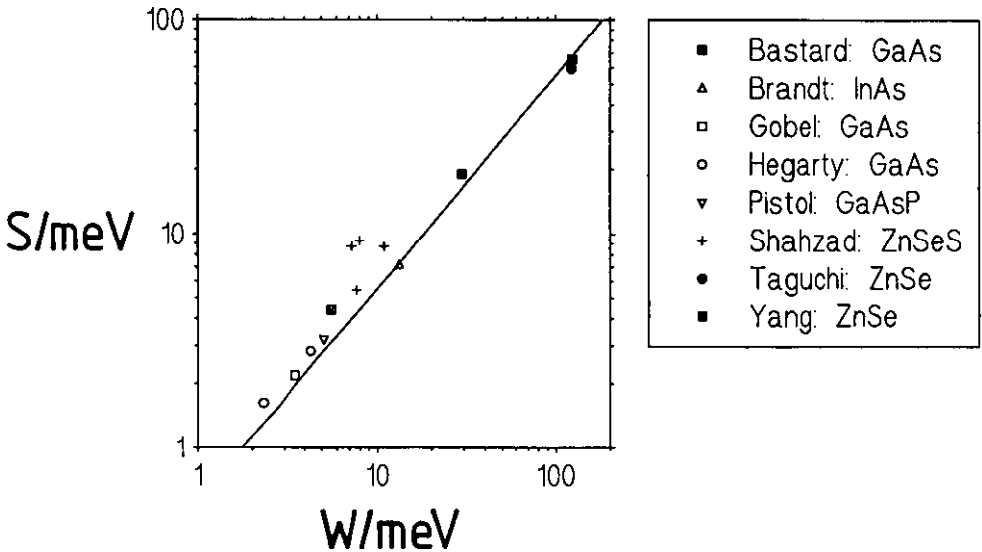


Figure 2. Plot of the offset of the peaks of the absorption and luminescence spectra, versus the full width at half-maximum of the former. The plot combines data for a variety of disordered 2D exciton systems, with different growth techniques, layer widths and direct gap semiconductors. For brevity only the first authors of the source papers are indicated. The straight line is our theoretical prediction.

proportional to the distribution of the heights of minima of this function. In section 3 we compute the distribution of heights of minima for a Gaussian random function. We find that the results depend on the spatial correlation function via a single dimensionless parameter. In section 4 we introduce a physical model for the spatial correlation of the exciton energy, and compare the results with experimental data.

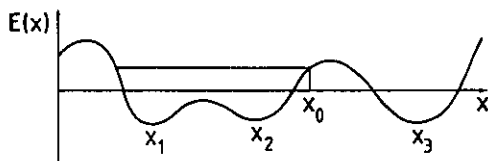


Figure 3. Representative plot of a Gaussian random function, showing local minima. An exciton created at position x_0 could be trapped in local minima at x_1 or x_2 , but not at x_3 .

We find reasonably good agreement, indicated by the theoretical line in figure 2. The theory described in section 3 gives the unweighted distribution of heights of minima: in section 5 we introduce a refinement of the model which weights each minimum according to the probability that it will trap an exciton. The results are close to those from the unweighted distribution of minima.

2. A statistical model for the luminescence spectrum

First we consider the form of the absorption peak. In the absence of disorder the peak would be very sharp, because (unlike for unbound electron-hole pairs) conservation of momentum implies that the exciton can only be created with one energy. Because the photon carries little momentum, the exciton is created very close to the bottom of its band. The widths of the absorption peaks in figure 1 are determined by inhomogeneous broadening due to disorder. The energy of an exciton in the ground state depends upon the width of the potential well in which it is confined, and the well width varies randomly with position in the plane. We assume that the length scale over which the well width varies is long compared to the width L of the wells: this implies that the ground state energy of a static exciton at position (x, y) is a well defined smooth function, which we denote by $E(x, y)$.

There is also a contribution to the inhomogeneous broadening due to fluctuations in the local composition of the semiconductor alloys from which the layers are built up. Bulk alloys usually show much smaller broadening than the multilayer systems which we consider (typically a few meV as opposed to several tens of meV). We therefore regard the effect of the alloy fluctuations as negligible.

Many forms of disorder, including the specific model we discuss in section 4, will give rise to fluctuations δL in the well width which are Gaussian distributed. If we also assume that the typical fluctuations in the well width are small compared to the mean value, the energy function $E(x, y)$ will also have Gaussian statistics. The level height of the function $E(x, y)$ will therefore be assumed Gaussian distributed, with probability distribution

$$P(E) = (1/\sqrt{2\pi}\sigma) \exp[-(E - \bar{E})^2/2\sigma^2] \quad (2.1)$$

If the potential is sufficiently slowly varying, an exciton can only be created at position (x, y) with the negligible centre of mass momentum provided by the incoming photon, and will therefore have energy $E(x, y)$. If the incoming radiation has a continuous

spectrum, with uniform intensity in the region of the exciton absorption line, the probability of an exciton being created at (x, y) is independent of position. Equation (2.1) therefore also describes the sharp peak in the absorption spectrum.

Now we consider the luminescence peak. This is shifted toward lower energies because the excitons can lose energy before they decay. Time-resolved studies of spectral hole burning indicate that the energies of excitons can change over a timescale of typically 20 ps, much shorter than the half-life for decay of excitons, typically 800 ps (Hegarty and Sturge 1985). The predominant mechanism of energy loss for the excitons appears to be by the excitation of phonons: if the absorption spectrum is probed with narrow spectral lines, it is possible to observe features in the luminescence spectrum which are shifted from the probe frequency by multiples of the frequency of the optical phonons (O'Donnell and Henderson 1992). These results lead to the following picture of the luminescence process: after the exciton is created at position (x_0, y_0) with energy $E_0 = E(x_0, y_0)$, it will move into regions where the potential energy $E(x, y)$ is less than E_0 , and the excess energy $E_0 - E(x, y)$ appears as kinetic energy. The moving exciton is able to excite phonons, and as it does so it loses kinetic energy. Eventually, if it does not decay in the meantime, it will end up trapped in a local minimum of the potential energy $E(x, y)$ (see figure 3). Because the exciton lifetime is much longer than the timescale associated with energy transfer to phonons, most of the excitons are trapped close to a local minimum of the potential energy $E(x, y)$ when they decay.

We assume a purely classical model for the localization of the excitons, i.e. we assume that the excitons do not tunnel out of local minima, and that the energy of a trapped exciton is equal to the energy of the minimum, implying that the zero-point energy of the centre of mass degree of freedom of the exciton is negligible. In the appendix we show that these assumptions are valid in the limit where the correlation length of the fluctuations in the well width is large compared to the well width. We also consider in greater depth the distinction between the type of disorder considered here (a smooth variation of the well widths), and the short-ranged substitutional alloy disorder which leads to Lifshitz tails in the density of states (Lifshitz 1967). Some of the experimental literature on the relationship between absorption and luminescence spectra in semiconductor alloys is also discussed in the appendix.

According to our model the luminescence spectrum is proportional to the distribution of heights of minima of $E(x, y)$, with each minimum weighted according to the probability that it will trap an exciton. The trapping probability depends on the exact details of the model for the loss of energy of the excitons, and for the sake of simplicity we initially assume that the mean probability for a minimum to trap an exciton is independent of the height of the minimum. We will therefore assume that the luminescence spectrum is proportional to the (unweighted) distribution of heights of minima. This assumption reduces the problem of finding the luminescence spectrum to a purely geometrical problem, that of finding the distribution of heights of minima of an isotropic Gauss random function in two dimensions.

The problem of counting minima of Gaussian random functions of one variable was considered by Rice (1945) in a theoretical analysis of electrical noise. An extension of the method to counting the stationary points of a two dimensional Gaussian random function was described by Longuet-Higgins (1957a, b), in the context of studies of the surface of the ocean, and references to further applications to the surfaces of materials and tribology can be found in an article by Greenwood (1984). Lukes and Tripath (1978) have considered an application of the theory of Gauss

random functions to the problem of Anderson localization in the band tail. None of these works contains a calculation of the result we require here, namely the probability density for the heights of minima of a statistically isotropic function in two dimensions, and we therefore give a fairly detailed calculation below.

3. Distribution of heights of minima

Consider the problem of computing the number of minima per unit area for a random function $f(x, y)$. We assume that the joint probability distribution $P(f, f_x, f_y, f_{xx}, f_{yy}, f_{xy})$ of the function f , its first derivatives $f_x = \partial f / \partial x$, $f_y = \partial f / \partial y$, and its second derivatives f_{xx}, f_{yy}, f_{xy} at a given point (x, y) is known. Let $\mathcal{N}(f) df$ be the number of minima of $f(x, y)$ per unit area with the height of the minimum between f and $f + df$. We can compute $\mathcal{N}(f)$ as follows: if δP is the probability that a minimum of the function with height between f and $f + df$ lies within an infinitesimal circle of radius δR surrounding the point (x, y) , then

$$\mathcal{N}(f) df = \delta P / \pi \delta R^2. \tag{3.1}$$

Assuming that a stationary point ($f_x = f_y = 0$) does indeed lie close to (x, y) , the displacement $\delta x = (\delta x, \delta y)$ of this point from (x, y) is given by

$$\begin{pmatrix} \delta x \\ \delta y \end{pmatrix} = -\tilde{\mathbf{M}}^{-1} \begin{pmatrix} f_x \\ f_y \end{pmatrix} \tag{3.2}$$

where $\tilde{\mathbf{M}}$ is the matrix of second derivatives

$$\tilde{\mathbf{M}} = \begin{pmatrix} f_{xx} & f_{xy} \\ f_{xy} & f_{yy} \end{pmatrix} \tag{3.3}$$

and f_x, f_y are the values of the derivatives evaluated at our test point (x, y) . From (3.2), we see that for a given matrix $\tilde{\mathbf{M}}$, there is an elliptical region in the space of f_x, f_y values such that $\delta x^2 + \delta y^2 < \delta R^2$. This region is centred on the origin and has area

$$\delta A = \frac{\partial(f_x, f_y)}{\partial(\delta x, \delta y)} \pi \delta R^2 = \pi \delta R^2 D \tag{3.4}$$

where $D = \det(\tilde{\mathbf{M}}) = f_{xx} f_{yy} - f_{xy}^2$. The probability of finding a stationary point with height between f and $f + df$ within a radius δR is therefore

$$\delta P = \pi \delta R^2 df \int_{-\infty}^{\infty} df_{xx} \int_{-\infty}^{\infty} df_{yy} \int_{-\infty}^{\infty} df_{xy} D P(f, 0, 0, f_{xx}, f_{yy}, f_{xy}). \tag{3.5}$$

This expression can be combined with (3.1) to give an expression for the density of stationary points. In order to get an expression for the density of minima, it is necessary to exclude areas where either of the eigenvalues of $\tilde{\mathbf{M}}$ is negative from the region of integration in f_{xx}, f_{yy}, f_{xy} space. A condition for both eigenvalues to be

positive is $D = \det(\tilde{\mathbf{M}}) > 0$, $T = \text{tr}(\tilde{\mathbf{M}}) > 0$. The density of minima can therefore be written in the form

$$\mathcal{N}(f) = \int_{-\infty}^{\infty} df_{xx} \int_{-\infty}^{\infty} df_{yy} \int_{-\infty}^{\infty} df_{xy} P(f, 0, 0, f_{xx}, f_{yy}, f_{xy}) D\Theta(D)\Theta(T) \quad (3.6)$$

where $T = \text{tr}(\tilde{\mathbf{M}}) = f_{xx} + f_{yy}$, and $\Theta(x)$ is the unit increasing step function.

We now consider how to evaluate this density of minima for a Gaussian random function with isotropic statistics. We can assume without loss of generality that the mean value of the function is zero. A Gaussian random function of two variables, $f(x, y)$ with mean value zero can be generated by convolution of a white noise function $W(x, y)$ with a smoothing function $F(x, y)$:

$$f(x, y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx' dy' F(x - x', y - y') W(x', y'). \quad (3.7)$$

The white noise function is defined by the properties

$$\langle W(x, y) \rangle = 0 \quad \langle W(x, y)W(x', y') \rangle = \delta(x - x')\delta(y - y') \quad (3.8)$$

where the angle brackets denote either an ensemble or a spatial average. In the context of the problem considered in this paper it is natural to assume that the statistical properties of $f(x, y)$ are isotropic: this can be obtained by choosing the smoothing function F to be a function of $r = (x^2 + y^2)^{1/2}$ only, i.e. $F(x, y) = F(r)$. The statistics of the Gaussian random function $f(x, y)$ can also be specified using the correlation function $c(\mathbf{R})$ or the power spectrum $S(\mathbf{k})$, which are related to the smoothing function $F(r)$ as follows

$$\begin{aligned} c(\mathbf{R}) &\equiv \langle f(\mathbf{r} + \mathbf{R})f(\mathbf{r}) \rangle = \int \int d\mathbf{r} F(\mathbf{r} + \mathbf{R})F(\mathbf{r}) \\ S(\mathbf{k}) &\equiv (1/V)|\bar{f}(\mathbf{k})|^2 = |\bar{F}(\mathbf{k})|^2 \end{aligned} \quad (3.9)$$

where $\bar{f}(\mathbf{k})$ and $\bar{F}(\mathbf{k})$ are the Fourier transforms of $f(\mathbf{r})$ and $F(\mathbf{r})$, and V is the area of the region. Because of isotropy, c and S are functions of $R = |\mathbf{R}|$ and $k = |\mathbf{k}|$ only.

In order to utilize (3.6) we will require the joint probability distribution function of the function and its first and second derivatives. A standard result shows that the joint probability distribution of a set of N correlated Gaussian random variables $(X_1, \dots, X_N) = \mathbf{X}$ is given by

$$P(X_1, \dots, X_N) = [(2\pi)^N \det(\tilde{\mathbf{C}})]^{-1/2} \exp\left(-\frac{1}{2}\mathbf{X}^T \tilde{\mathbf{C}}^{-1} \mathbf{X}\right) \quad (3.10)$$

where $\tilde{\mathbf{C}}$ is the covariance matrix, with elements

$$C_{ij} = \langle X_i X_j \rangle. \quad (3.11)$$

The elements of the covariance matrix can be expressed in terms of moments of the power spectrum $\bar{S}(k)$, for example:

$$\begin{aligned} \langle f(x, y) f_{xx}(x, y) \rangle &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx' dy' F(x', y') \frac{\partial^2 F}{\partial x^2}(x', y') \\ &= - \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y k_x^2 |\bar{F}(\mathbf{k})|^2 \\ &= -2\pi \int_0^{\infty} dk \int_0^{2\pi} d\theta \cos^2 \theta k^3 S(k) = -\pi \int_0^{\infty} dk k^3 S(k). \end{aligned} \quad (3.12)$$

We can assume that the following conditions hold without any loss of generality

$$\langle f \rangle = 0 \quad \langle f^2 \rangle = 1 \quad \langle f_x^2 \rangle = \langle f_y^2 \rangle = 1. \tag{3.13}$$

These conditions can always be satisfied by scaling f , x and y respectively. For an isotropic function satisfying (3.13), we find (by means of computations similar to (3.12)) that the following relationships exist between the correlations of the function and its derivatives:

$$\begin{aligned} \langle f_{xx}^2 \rangle = \langle f_{yy}^2 \rangle = 3\langle f_{xy}^2 \rangle = 3\langle f_{xx}f_{yy} \rangle & \quad \langle f_{xx}f_{xy} \rangle = \langle f_{yy}f_{xy} \rangle = 0 \\ \langle ff_{xx} \rangle = \langle ff_{yy} \rangle = -1 & \quad \langle ff_{xy} \rangle = 0. \end{aligned} \tag{3.14}$$

If we choose the elements of the vector $X = (X_1, \dots, X_6)$ in (3.10) as follows,

$$\begin{aligned} X_1 = f & \quad X_2 = f_x & \quad X_3 = f_y & \quad X_4 = \frac{1}{2}(f_{xx} + f_{yy}) \\ X_5 = \frac{1}{2}(f_{xx} - f_{yy}) & \quad X_6 = f_{xy} \end{aligned} \tag{3.15}$$

then the covariance matrix takes the nearly diagonal form

$$\tilde{C} = \begin{pmatrix} 1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 2a & 0 & 0 \\ 0 & 0 & 0 & 0 & a & 0 \\ 0 & 0 & 0 & 0 & 0 & a \end{pmatrix} \tag{3.16}$$

where we have written

$$a = \langle f_{xy}^2 \rangle. \tag{3.17}$$

Note that $D = X_4^2 - X_5^2 - X_6^2$ and that $T = 2X_4$, so that the region of integration selected by the step functions in (3.6) is a cone in X_4, X_5, X_6 space, with vertex at the origin, with its principal axis along the X_4 axis. In the X_i variables, only $X_1 = f$ and $X_4 = \frac{1}{2}T$ are correlated, and their joint distribution function is

$$p(f, X_4) = \frac{1}{2\pi\sqrt{2a-1}} e^{-f^2/2} \exp\left[-\frac{(f + X_4)^2}{2(2a-1)}\right]. \tag{3.18}$$

The density of minima is therefore

$$\mathcal{N}(f) = \frac{1}{(2\pi)^2 a} \int_0^\infty dR p(f, R) \int \int_{\mathcal{A}} dx dy (R^2 - x^2 - y^2) e^{-(x^2+y^2)/2a} \tag{3.19}$$

where \mathcal{A} is the disc $x^2 + y^2 < R^2$, and for clarity we have changed the names of X_4, X_5, X_6 to R, x, y . Calculating the integral over \mathcal{A} in polar coordinates gives

$$\mathcal{N}(f) = \frac{1}{2\pi} \int_0^\infty dR p(f, R) [R^2 + 2a(e^{-R^2/2a} - 1)]. \tag{3.20}$$

Combining (3.18) and (3.20) we obtain a formula for $\mathcal{N}(f)$ in the form of an integral, depending on a single parameter a . The integral can be evaluated analytically using some results from Gradshteyn and Ryzhik (1980): the result is

$$\begin{aligned} \mathcal{N}(f) = & \frac{1}{(2\pi)^2 \sqrt{2a-1}} \left[-(2a-1)f \exp\left(\frac{-af^2}{(2a-1)}\right) \right. \\ & + \frac{a\sqrt{2\pi a(2a-1)}}{\sqrt{3a-1}} \exp\left(\frac{-3af^2}{2(3a-1)}\right) \operatorname{erfc}\left(\sqrt{\frac{a}{2(2a-1)(3a-1)}} f\right) \\ & \left. - \frac{1}{2}\sqrt{2\pi(2a-1)}(f^2-1) \exp(-f^2/2) \operatorname{erfc}\left(\frac{f}{\sqrt{2(2a-1)}}\right) \right] \quad (3.21) \end{aligned}$$

where $\operatorname{erfc}(x)$ is the complementary error function (Abramowitz and Stegun 1970). The probability distribution of heights of minima is obtained by dividing this function by its integral from $-\infty$ to ∞ , which has value

$$M_0(a) = a/(2\pi\sqrt{3}). \quad (3.22)$$

The mean and variance of the heights of the minima can also be computed analytically: the first and second moments of (3.21) are

$$M_1(a) = -\frac{8\sqrt{\pi a}}{3(2\pi^2)} \quad M_2(a) = \frac{1}{2\pi} \left(1 + \frac{3a-1}{3\sqrt{3}}\right) \quad (3.23)$$

which leads to the following surprisingly simple expressions for the mean $\mu(a)$ and variance $V(a)$ of the distribution

$$\mu(a) = \frac{-4}{\sqrt{3\pi a}} \quad V(a) = 1 + \frac{1}{a} \left(\sqrt{3} - \frac{16}{3\pi} - \frac{1}{3}\right). \quad (3.24)$$

The distribution of heights of minima is plotted in figure 4 for the case $a = 1$; we have not plotted other cases because the distribution of heights of minima resembles a Gaussian distribution quite closely for all values of a . For large a the distribution of heights of minima tends towards the Gaussian distribution of the function itself.

We have seen that in the case where the normalizations (3.13) are satisfied the distribution of minima depends on a single parameter a . In the general case where (3.13) does not hold, a is the following dimensionless combination of moments

$$a = \langle f_{xx}^2 \rangle \langle f^2 \rangle / (3 \langle f_x^2 \rangle^2). \quad (3.25)$$

For an isotropic random function the value of a is always greater than $\frac{1}{2}$: this lower limit obtains when the power spectrum $S(k)$ is sharply peaked at a non-zero value of k (i.e. when the function has a 'ring' spectrum). The parameter a only exists if $S(k)$ decays faster than k^{-6} .

4. Comparison with experimental data

The distribution of heights of minima was shown in section 3 to depend on the correlation function of the disorder through a single dimensionless parameter a ,

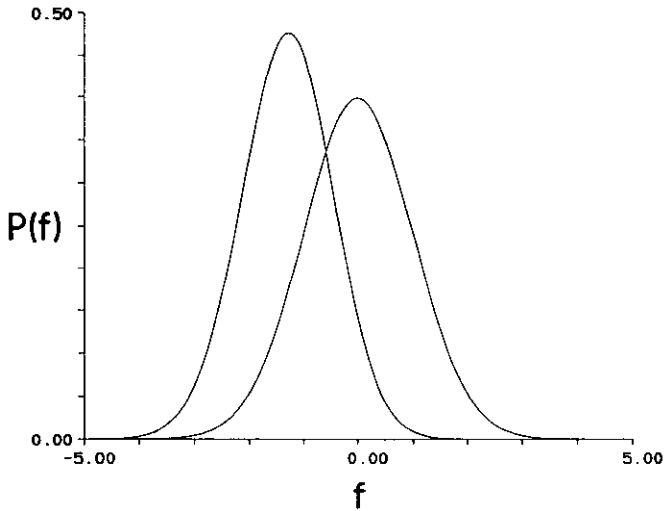


Figure 4. The probability distribution of heights of minima for a Gaussian random function, when the dimensionless parameter a is unity. The Gaussian distribution of the function itself is included for reference. These curves clearly resemble the pairs of spectra in figure 1.

defined by (3.25). In order to compare the theory with experimental results we must first consider the form of the spatial correlation function of the disorder. In this section we describe a physically reasonable model which predicts that the spatial correlation function will be a Gaussian for some types of samples. We will show that the theory is in reasonable agreement with experimental data if we assume a Gaussian spatial correlation function.

It is clear that surface diffusion must play a role in producing high-quality multiple-quantum-well semiconductor structures, because random deposition of atoms could not produce structures in which the well widths are defined to monolayer accuracies in the best samples. Experimental evidence for this comes from the fact that when multiple-quantum-well samples are grown, inhomogeneous broadening of the spectral lines is reduced if the sample is left for a period of time at a high temperature between growing layers of different materials: surface diffusion smoothes out any irregularities which have occurred in the process of building up the uppermost layer.

The observation that diffusion is important in the growth process suggests the following simple model for the correlation function of the well width fluctuations. The probability of a particle being displaced through a vector $\mathbf{r} = (x, y)$ into an element of area $dx dy$ by surface diffusion is

$$P_d(x, y) dx dy = [1/(8\pi\mathcal{D}t)] \exp[-(x^2 + y^2)/4\mathcal{D}t] dx dy \tag{4.1}$$

where \mathcal{D} is the diffusion constant. The density $\rho(x, y)$ of material at position (x, y) after the diffusion process is given by

$$\rho(x, y) = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' P_d(x - x', y - y') \rho_0(x', y') \tag{4.2}$$

where $\rho_0(x, y)$ is the density of material on the surface before diffusion is allowed to occur. Clearly $\rho_0(x, y)$ is a random function with unknown properties. If we assume

that this function either has no spatial correlations, or that its spatial correlations are very short ranged compared to \sqrt{Dt} , then ρ_0 can be modelled by a white noise function and (4.2) becomes analogous to (3.7). From (4.1) we see that the smoothing function is Gaussian, which implies that the spatial correlation function is therefore also a Gaussian. This is a reasonable model for the spatial correlations if the fluctuations in the layer width are much larger than a monolayer in width. Many samples have average effective layer width fluctuations of one monolayer or less: we do not have a theory for the spatial correlation function in these systems.

We have argued that for certain samples the correlation function is Gaussian, which leads to the value $a = 1$ for the dimensionless parameter in section 3. We now use this value for a in a comparison of the theoretical distribution (3.21) with some experimental data. In figure 2 we have summarized data from a wide range of experiments (Bastard *et al* 1984, Brandt *et al* 1992, Göbel 1988, Hegarty and Sturge 1985, Pistol and Liu 1992, Shahzad *et al* 1990, Taguchi 1990, Yang and O'Donnell 1992). We have plotted the ratio of the displacement S of the peaks of the spectra against the full width at half-maximum W of the absorption peak, and found that they are proportional: $S = \gamma W$. As well as data such as those shown in figure 1, which correspond quite closely to the idealized spectra shown in figure 4, we have also included data from some experiments where the lineshapes are asymmetric, due to luminescence from impurities. We included only measurements at temperatures low enough that kT is small compared to the linewidth σ . If we assume that the peak of the luminescence coincides with the mean value of the distribution of heights of minima, and that the absorption peak is a Gaussian with variance σ , the constant of proportionality is predicted to be

$$\gamma = |\mu(a)|/(2\sigma\sqrt{2\ln 2}) = 2/(\sqrt{6\pi\ln 2}a). \quad (4.3)$$

In the case of a Gaussian correlation function we have $a = 1$, so that

$$\gamma \approx 0.553. \quad (4.4)$$

A line has been drawn with this slope on figure 2, and gives a reasonably good fit to the data.

Our comparison with the experimental data has assumed a Gaussian form for the spatial correlation function. We note that other physically reasonable forms for the correlation function give similar values for γ , however. For example, if the smoothing function in (3.7) were a Lorentzian ($F(r) = 1/(A^2 + r^2)$), then we would have $a = 5/3$, which would only reduce the value of γ by 23%. The results are therefore fairly insensitive to the value of a , provided we confine ourselves to smooth, monotonically decreasing correlation functions.

5. A refinement of the model

In earlier sections of this paper we assumed that the probability of a minimum trapping an exciton is independent of its depth. In this section we consider a generalization and refinement of the model for which we can, in a limiting case, avoid making this assumption. We will address the following question. What is the luminescence intensity at energy E_1 in response to a monochromatic excitation of unit

intensity at energy E_2 ? We are able to give a precise answer to this question (apart from an unknown multiplicative constant) when $E_2 - E_1$ is small compared to the linewidth σ . The result of this analysis is independent of E_2 (provided $E_2 > E_1$). We speculate that even when $(E_2 - E_1)/\sigma$ is not small, the resulting function of E_1 may provide a more accurate theory for the luminescence spectrum than the unweighted distribution of heights of minima obtained in section 3.

According to the model described in section 2, the luminescence intensity in the energy range $E_1 < E < E_1 + dE_1$, given excitation of unit intensity concentrated in the energy range $E_2 < E < E_2 + dE_2$, will be proportional to the fraction of the area of the (x, y) plane for which $E_2 < E(x, y) < E_2 + dE_2$, and for which the particles created between these contours end up trapped in minima with depth E_0 in the range $E_1 < E_0 < E_1 + dE_1$. We call this fractional area $\Gamma(E_1, E_2) dE_1 dE_2$. In general it is extremely difficult to calculate $\Gamma(E_1, E_2)$ because, unlike the distribution of heights of minima, it depends on non-local properties of the function (such as which minima are enclosed by a given contour). Another complication is that, in general, $\Gamma(E_1, E_2)$ depends on the dynamical processes by which the excitons lose energy, as well as the topography of the energy surface $E(x, y)$.

When E_1 is close to E_2 , we can however determine $\Gamma(E_1, E_2)$ analytically, using the following argument. When this condition is satisfied, we can approximate the behaviour of the function $E(x, y)$ by a Taylor series expansion about the minimum at $E_0 \approx E_1$. The leading-order terms are a quadratic form in x and y :

$$E(x, y) = E_0 + \frac{1}{2}[f_{xx}(x - x_0)^2 + f_{yy}(y - y_0)^2 + 2f_{xy}(x - x_0)(y - y_0)] + \dots \tag{5.1}$$

If E_2 is only slightly greater than E_0 , the contour $E(x, y) = E_2$ contains an ellipse centred on (x_0, y_0) , and any particles created on this section of the contour are inevitably trapped by the minimum at (x_0, y_0) . The area enclosed by the elliptical contour at E_2 is

$$A = 2\pi(E_2 - E_1)/\sqrt{D} \tag{5.2}$$

where $D = f_{xx}f_{yy} - f_{xy}^2$. Differentiating (5.2) with respect to E_2 , we find that the contribution from this minimum to the fractional area $\Gamma(E_1, E_2) dE_1 dE_2$ is $2\pi dE_2/\sqrt{D}$. The fractional area $\Gamma(E_1, E_2) dE_1 dE_2$ is therefore the density of minima between E_1 and $E_1 + dE_1$, weighted by the area $2\pi dE_2/\sqrt{D}$ of the elliptical contour between E_2 and $E_2 + dE_2$ surrounding each minimum. The function $\Gamma(E_1, E_2)$ is therefore independent of E_2 in this approximation, provided $E_2 > E_1$: we can therefore write $\Gamma(E_1, E_2) = \Theta(E_2 - E_1)\Phi(E_1)$, where $\Theta(x)$ is the step function. The function $\Phi(E)$ is given by

$$\begin{aligned} \Phi(E) &= 2\pi \int_{-\infty}^{\infty} df_{xx} \int_{-\infty}^{\infty} df_{yy} \int_{-\infty}^{\infty} df_{xy} P(f, 0, 0, f_{xx}, f_{yy}, f_{xy}) D^{1/2} \Theta(D) \Theta(T) \\ &= \frac{1}{2\pi a} \int_0^{\infty} dR p(f, R) \int_0^{\infty} dr r \sqrt{R^2 - r^2} e^{-r^2/2a} \end{aligned} \tag{5.3}$$

where $p(f, R)$ is given by (3.18). This is similar to the density of minima given by (3.6), with the minima weighted by the factor $D^{-1/2}$, which gives less weight to minima for which the curvature at the minimum is large.

We have not succeeded in evaluating the weighted density of minima, $\Phi(E)$ analytically. Figure 5 shows the numerically computed distribution $\Phi(E)$ for the case

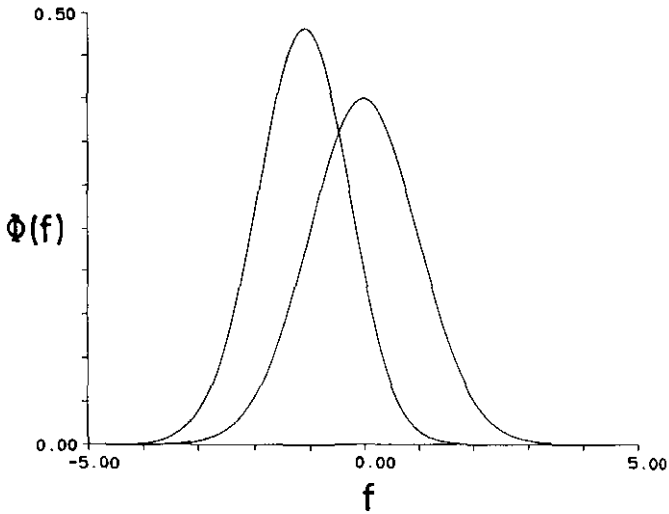


Figure 5. The weighted distribution of heights of minima $\Phi(E)$ of a Gauss random function when $a = 1$. The Gaussian distribution of the function is shown for reference.

$a = 1$, with the area under the curve normalized to unity. The mean and variance of $\Phi(E)$ are plotted as a function of a in figure 6. The weighted distribution $\Phi(E)$ is similar in form to the unweighted distribution, but the mean value is somewhat less negative: for instance when $a = 1$ the mean and variance are $\mu = -1.1104\dots$, $V = 0.6866\dots$, compared to $\mu = -1.3029\dots$, $V = 0.7011\dots$ for the unweighted distribution. The mean value is higher because the second derivatives f_{xx} , f_{yy} are inversely correlated with f , and the weighting function $D^{-1/2}$ is a decreasing function of these second derivatives.

6. Conclusions

We have pointed out a nearly universal relationship between the exciton absorption and luminescence spectra of semiconductor quantum-well systems: the absorption spectrum is close to Gaussian in form, and the luminescence spectrum is similar in shape, but shifted to lower energies by approximately one standard deviation.

We have explained these results in terms of a model in which the energy E of a stationary exciton at position (x, y) is assumed to be a Gaussian random function. The Gaussian absorption peak is explained by assuming that the exciton is created at a random position in the (x, y) plane. The shift of the luminescence peak is explained by the fact that the excitons lose energy by excitation of phonons. This occurs on a timescale much shorter than the lifetime of the excitons, and by the time the excitons decay, most of them are sitting in minima of the random function $E(x, y)$. We can therefore model the luminescence spectrum by the distribution of minima of a Gaussian random function.

In section 3 we calculated the distribution of heights of minima of an isotropic Gauss random function. We found that the distribution depends on one dimensionless parameter characterizing the spatial correlation function. Although the distribution is a very complicated function, the analytical formulae for the mean and variance are

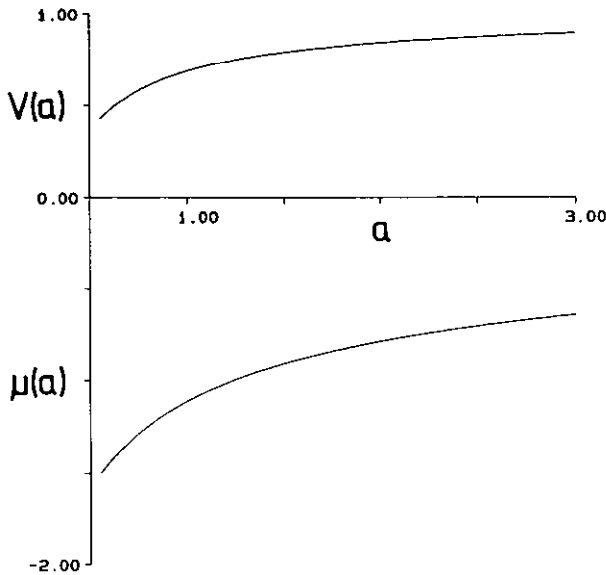


Figure 6. The mean (lower curve) and variance of the weighted distribution $\Phi(E)$ of heights of minima, as a function of the dimensionless parameter a .

remarkably simple. In section 4 we argued that the spatial correlation function is determined by surface diffusion processes during the growth of the sample: a simple model for this leads to the prediction that the correlation function is Gaussian. The 'Stokes shift' of the luminescence peak predicted by this model is in good agreement with the observed value, although the lineshapes are only in qualitative agreement with the theory. For physically reasonable correlation functions the distribution of minima is not very sensitive to the value of the dimensionless parameter a . A more detailed comparison with experimental results would require more information on the spatial correlation function of fluctuations of the well widths.

In section 5 we described a refinement of the model, which takes account of the fact that different minima have different probabilities of trapping excitons, depending on the curvature of the function in the region of the minimum. The results are similar to those for the unweighted distribution of minima.

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Appendix

The purpose of this appendix is to clarify the conditions under which the classical localization model of section 2 is valid, and to distinguish them from the conditions under which the bottom of the exciton spectrum would be expected to exhibit 'Lifshitz tails'. The condition for classical localization will be expressed in terms of an

inequality involving purely geometrical properties of the quantum wells (equation (A4)).

Consider the creation of excitons in a system without disorder. In this case conservation of momentum implies that the momentum of the centre of mass degrees of freedom of the exciton must equal that of the incoming photons. The photon wavenumber is very small compared to the width of the Brillouin zone, implying that the excitons are all created with one energy, which is effectively the bottom of the exciton band.

We have considered disorder in the form of a random variation of the width L of the potential wells (i.e. of the layers of lower-bandgap material). We assume that the well widths are a smooth function of position (x, y) in the plane of confinement, with a correlation length λ . The energy $E(x, y)$ of a stationary exciton is therefore a random function with correlation length λ . The model considered in section 2 assumes that the exciton can be localized classically in minima of $E(x, y)$, and that the width of the absorption peak is determined by the standard deviation σ of the distribution function of $E(x, y)$. We now consider the conditions under which both of these assumptions are valid.

We can use classical considerations to analyse the localization of the excitons if the depth of a typical minimum, which is of order σ , is large compared to the zero-point energy of an exciton trapped in the minimum. The linear extent of a minimum is of order λ , implying that a particle oscillating in the (x, y) plane about the minimum has a classical frequency of order $\omega \sim \sqrt{\sigma/m\lambda^2}$. The zero-point energy $\hbar\omega$ is therefore:

$$\delta E_0 \sim (\hbar/\lambda)\sqrt{\sigma/m}. \quad (\text{A1})$$

We find that $\delta E_0 \ll \sigma$ if the following inequality is satisfied

$$\lambda\sqrt{m\sigma} \gg \hbar. \quad (\text{A2})$$

It is informative to convert (A2) into an inequality involving δL . The confinement energy of a particle in a potential well is $E_c \sim \hbar^2/mL^2$. The relationship between the fluctuations of E of size σ and those of L is therefore

$$\sigma \sim (\hbar^2/mL^2) \delta L/L. \quad (\text{A3})$$

Using (A3), the inequality (A2) expressing the condition for classical localization can be expressed purely in terms of geometrical quantities:

$$\lambda^2 \delta L \gg L^3. \quad (\text{A4})$$

Next consider the width of the absorption peak. One contribution to the width of this peak comes from the standard deviation σ of the energy function $E(x, y)$. This must be compared with another contribution: in the presence of disorder, excitons may be created with a range of centre of mass momenta $\delta p \sim \hbar/\lambda$ (where λ is the correlation length of the disorder). This gives a contribution to the width of the exciton absorption peak of size

$$\delta E_p \sim \hbar^2/m\lambda^2. \quad (\text{A5})$$

Using (A3) we can rewrite (A5) in the form

$$\delta E_p \sim (L^3/\lambda^2 \delta L) \sigma. \quad (\text{A6})$$

It is now clear that $\delta E_p \ll \sigma$ if the inequality (A4) is satisfied. We have seen that if (A4) is satisfied, the excitons are classically localized, and that the width of the absorption peak is determined by the range of fluctuations of $E(x, y)$.

An important source of disorder in most of the materials we have considered is substitutional alloy disorder: we have ignored the effects of local fluctuations in the composition of the crystal lattice, implicitly assuming that the effects of the well width fluctuations are dominant. The correlation length of the substitutional alloy disorder is very short (comparable to the atomic spacing). In the case of very short-ranged disorder our classical localization model does not apply. The problem of Anderson localization at the band edges for a potential with short-ranged correlations has been treated by Lifshitz (1967), and Halperin and Lax (1966). They show that the density of states near the edge of the band has a distinctive non-Gaussian tail, with a universal functional form. The development of a theory for the 'Stokes shift' of the exciton spectrum appears to be difficult for this case.

Experiments on bulk semiconductor alloys have indicated linear relationships between the 'Stokes shift' of the luminescence spectrum and the inhomogeneous broadening of the absorption spectrum, which are analogous to the relationship we have discovered in multilayer systems. In bulk alloys it is found empirically that the lower edge of the absorption profile obeys 'Urbach's rule' (Urbach 1953): the absorption coefficient is given by

$$\alpha(\omega) = \alpha_0 \exp(\omega/\omega_s). \quad (\text{A7})$$

Permogorov and Reznitsky (1992) have found that the ratio of the offset S of the photoluminescence and absorption peaks to the Urbach parameter ω_s is approximately 5.0 in many bulk semiconductor alloys. Naumov *et al* (1990) have found that the ratio of the exciton absorption linewidth W to ω_s is approximately 2.6. Combining these results we find that $\gamma = S/W$ is approximately 1.9 for the bulk alloys. This is considerably larger than the value $\gamma \sim 0.6$ we observed in multilayer systems, indicating that the origin of the Stokes shift is different in these systems.

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