On the theory of the Franz–Keldysh effect

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Abstract. The excitonic optical absorption in the presence of a static electric field has been evaluated by solving the effective mass equation numerically. The results are compared with a previous approximate calculation and some experimental measurements. A certain degree of agreement has been found with experiment.

1. Introduction

A theory of optical absorption near the gap energy by insulating crystals in the presence of static electric field was first developed by Franz (1958) and Keldysh (1958). Using Houston (1940) wave functions they found that the absorption threshold is moved to lower energies, and that the absorption curve on the low-energy side of the zero-field threshold has the form of an exponential tail.

Callaway (1963, 1964) and Tharmalingam (1963) have extended these calculations, using known properties of the Airy function, to obtain the form of the absorption curve over as much of the spectrum as is well described by the effective mass approximation. They found the exponential tail already known and some oscillations above the zero-field threshold. Penchina (1965) has extended Tharmalingam's calculations to cover the case of indirect absorption. Callaway's calculations have been extended by Callaway and Viswanathan (1966) who have discussed the dielectric constant near the threshold while Seraphin and Bottka (1965) have discussed the effect of an electric field on the refractive index and have applied their results to the change in reflectivity. Phillips (1966) has discussed the effect of an electric field near saddle-point edges.

All these calculations have assumed that the independent particle approximation holds, and so are applicable only to the situation where the energy of the electron–hole pair in the field is much larger than the maximum exciton binding energy. Because of the large dielectric constants and the small effective masses often met particularly in semiconductors, a field sufficiently large to fulfil this condition is easily obtained. It is, however, of interest to analyse the system when the energy of the pair in the field is of the same order as their mutual energy.

The first attempt to take account of the electron–hole interaction seems to have been made by Duke (1965, see also Duke and Alferieff 1966) who finds an analytic solution to an equation which is similar to the effective mass equation with both a field term and a Coulomb term.

It should be mentioned here that a perturbation expansion in powers of the field cannot be expected to give the correct results because the width Γ of an absorption line for small fields is given by

$$\Gamma = A \exp\left(\frac{B}{F}\right) \tag{1}$$

using the WKB approximation where F is the field strength and A and B are constants and cannot be expressed in a Taylor series expansion in F about zero field.

2. Optical absorption in the effective mass approximation

The expression for the absorption coefficient K has been set down many times (e.g. Elliott 1963);

$$K_{\mathrm{A}} = \frac{2\pi e^2}{m^2 c \eta' \nu} |U(0)|^2 \langle c\mathbf{k}_0|\boldsymbol{\epsilon} \cdot \mathbf{p}|v\mathbf{k}_0\rangle^2 |S(h\nu) \tag{2a}$$

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for the allowed case and

$$K_F = \frac{2\pi e^2 \hbar^2}{m^4 c \eta' \nu} |\nabla U(0) \cdot \langle \mathbf{ck}_0 | \mathbf{M} | \mathbf{vk}_0 \rangle|^2 S(h\nu) \tag{2b}$$

for the forbidden case where $U(\mathbf{r})$ is the solution of the effective mass equation in relative coordinates $\mathbf{r}$, $\mathbf{k}_0$ is the point in $\mathbf{k}$ space where the minimum energy gap between the conduction band c and the valence band v occurs, $S(h\nu)$ is the density of excited states at the photon energy $h\nu$ above the ground state, η' is the real part of the refractive index function at the frequency ν, and e, m and c have their usual meetings. M is the operator

$$M = \sum_i \left(\frac{\mathbf{p}|i\rangle\langle i|\boldsymbol{\epsilon} \cdot \mathbf{p}}{E_c - E_i} + \frac{\boldsymbol{\epsilon} \cdot \mathbf{p}|i\rangle\langle i|\mathbf{p}}{E_v - E_i} \right) \tag{2c}$$

where $\boldsymbol{\epsilon}$ is the polarization, and the sum is over all bands except c and v.

The effective mass equation is

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{\kappa r} + eFz \right) U(\mathbf{r}) = EU(\mathbf{r}) \tag{3}$$

where μ is the reduced effective mass $m_e m_h/(m_e + m_h)$, E is the energy from the bottom of the conduction band, κ is a dielectric constant and F is the field strength. If units are chosen so that both the exciton rydberg

$$R = \frac{\mu e^2}{2\hbar^2 \kappa^2} \tag{4a}$$

and the exciton Bohr radius

$$a = \frac{\hbar^2 \kappa}{\mu e^2} \tag{4b}$$

are unity, the effective mass equation (3) becomes

$$\left(-\nabla^2 - \frac{2}{r} + fz \right) U = EU \tag{5}$$

where the field strength f is measured in rydbergs per Bohr radius.

Because of the removal of spherical symmetry by the introduction of the electric field, equation (5) is not separable in spherical polar coordinates, but it is still separable in parabolic coordinates defined by

$$\xi = r + z \tag{6a}$$

$$\zeta = r - z \tag{6b}$$

$$\phi = \phi. \tag{6c}$$

These coordinates are well discussed in standard textbooks (e.g. Morse and Feshbach 1953). The solution of the effective mass equation (5) may be written in the form

$$U(\mathbf{r}) = \frac{\chi_1(\xi)\chi_2(\zeta)\,e^{im\phi}}{(\xi\zeta)^{1/2}} \tag{7}$$

where the χ_i are solutions of the equations

$$\chi_1'' + \left(\frac{1-m^2}{4\xi^2} + \frac{t}{\xi} + \frac{E}{4} - \frac{f\xi}{8} \right)\chi_1 = 0 \tag{8a}$$

$$\chi_2'' + \left(\frac{1-m^2}{4\zeta^2} + \frac{1-t}{\zeta} + \frac{E}{4} + \frac{f\zeta}{8} \right)\chi_2 = 0 \tag{8b}$$

where t is a separation parameter.

These equations are in a convenient form for numerical integration using Numerov's method (e.g. see Hartree 1958).

The solutions can be classified using the energy, the angular quantum number m and the number of zeros $p-1$ in the function $\chi_1(\xi)$. It is easy to see that the only wave functions which have a finite value at the origin have m zero and those with a finite slope have m one or zero. Solutions with large values of p give small contributions to the optical absorption because they correspond to a large value of the separation constant t for which a large barrier develops in the potential of equation (8b) preventing the particle from penetrating to the origin. Experience shows that only a very few solutions are needed.

The solution of equation (8a) defines values of t and p with which the function χ_2 may be found. The asymptotic form of χ_2 is

$$\chi_2(\zeta) \to \frac{A}{(E/f+\zeta/2)^{1/4}} \sin\left\{\tfrac{2}{3}f^{1/2}\left(\frac{E}{f}+\frac{\zeta}{2}\right)^{3/2}+\eta\right\} \tag{9}$$

for some constant A as ζ approaches infinity, where η varies only logarithmically with ζ. The density of states is found by assuming that the function is zero at some point $\zeta = L$, where the argument of the sine must then be $n\pi$. The density of states turns out to be

$$S(E) = \frac{dn}{dE}\frac{1}{} = \frac{1}{\pi}\left(\frac{L}{2f}\right)^{1/2} \tag{10}$$

for large L.

The normalization constant I is easily evaluated from

$$I^2 = \int |U|^2 J\, d\xi\, d\zeta\, d\phi \tag{11}$$

where the Jacobian J is

$$J = \tfrac{1}{4}(\xi+\zeta). \tag{12}$$

The integral (11) has two terms from (12), the first of which is the less divergent and may be neglected giving for the normalization constant

$$I^2 = \pi A^2 (\tfrac{1}{2}d)^{1/2} \int_0^\infty \frac{\chi_1^2}{\xi}\, d\xi. \tag{13}$$

The power series expansion of the χ_i about the origin are

$$\chi_1 = \xi^{(|m|+1)/2}\left\{1 - \frac{t}{|m|+1}+O(2)\right\} \tag{14a}$$

$$\chi_2 = \zeta^{(|m|+1)/2}\left\{1 - \frac{1-t}{|m|+1}+O(2)\right\} \tag{14b}$$

so that the wave function from equation (7) becomes

$$U(\mathbf{r}) = (x^2+y^2)^{|m|}\left\{1 + \frac{(1-2t)z-r}{|m|+1}+O(2)\right\} e^{im\phi}. \tag{15}$$

The value of U at the origin is unity if m is zero, and zero otherwise, giving for the allowed absorption coefficient from equations (2a), (10) and (15)

$$K_\mathrm{A} = \frac{2\pi e^2}{m^2 c\eta'\nu}\frac{|\langle c\mathbf{k}_0|\boldsymbol{\epsilon}\cdot\mathbf{p}|v\mathbf{k}_0\rangle|^2}{A^2\pi^2 f^{1/2}\int_0^\infty (\chi_1^2/\xi)\,d\xi}. \tag{16}$$

In the forbidden case there are two possibilities with the light polarization either parallel or perpendicular to the field. For the states with m zero $U(\mathbf{r})$ has a slope only in the z
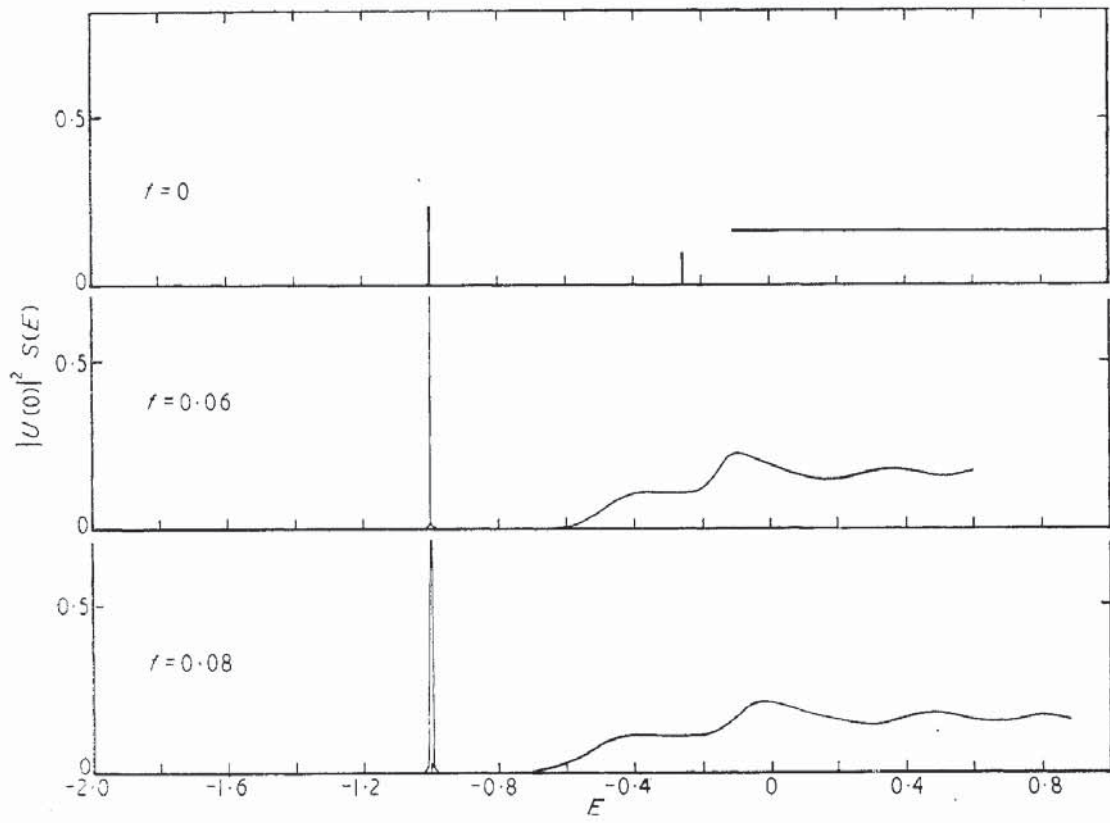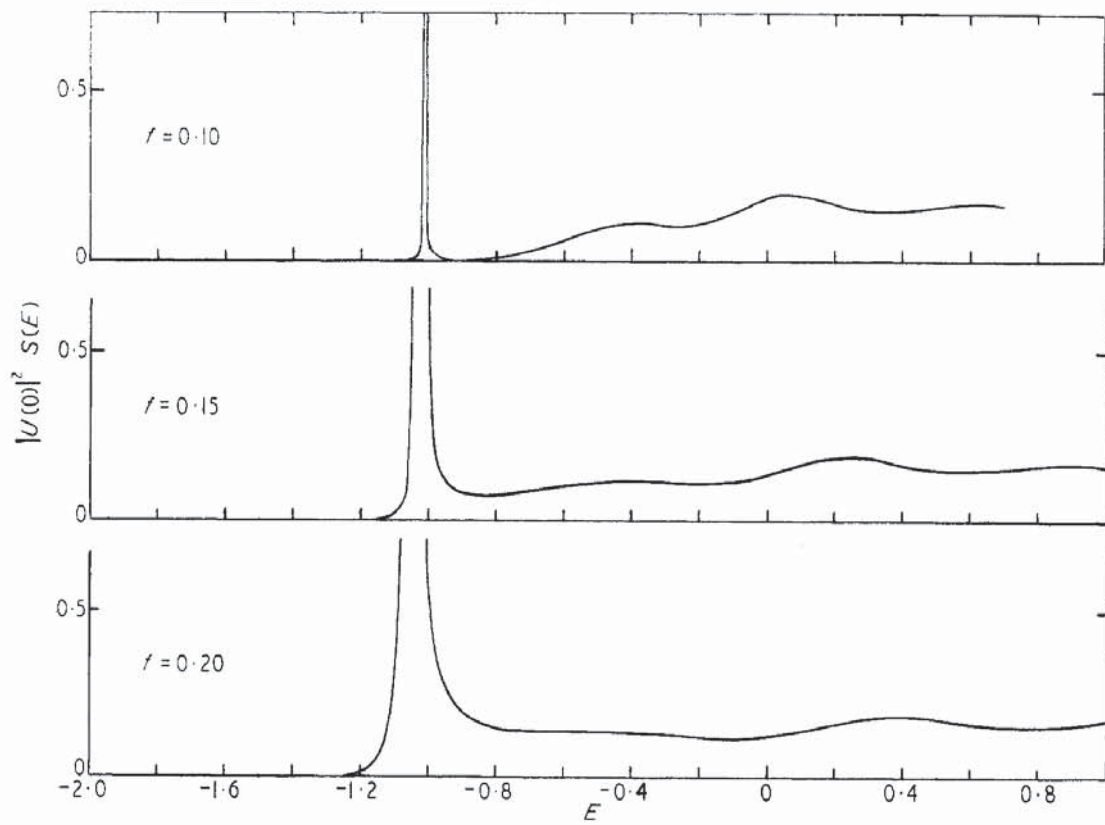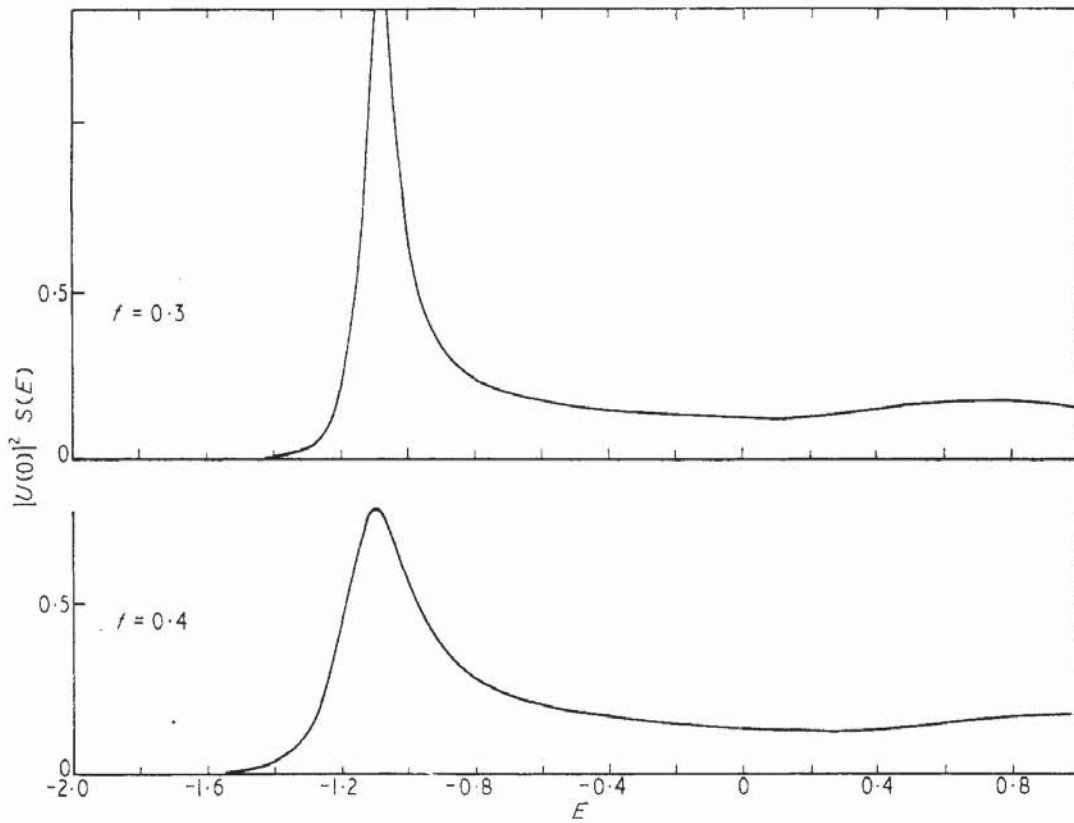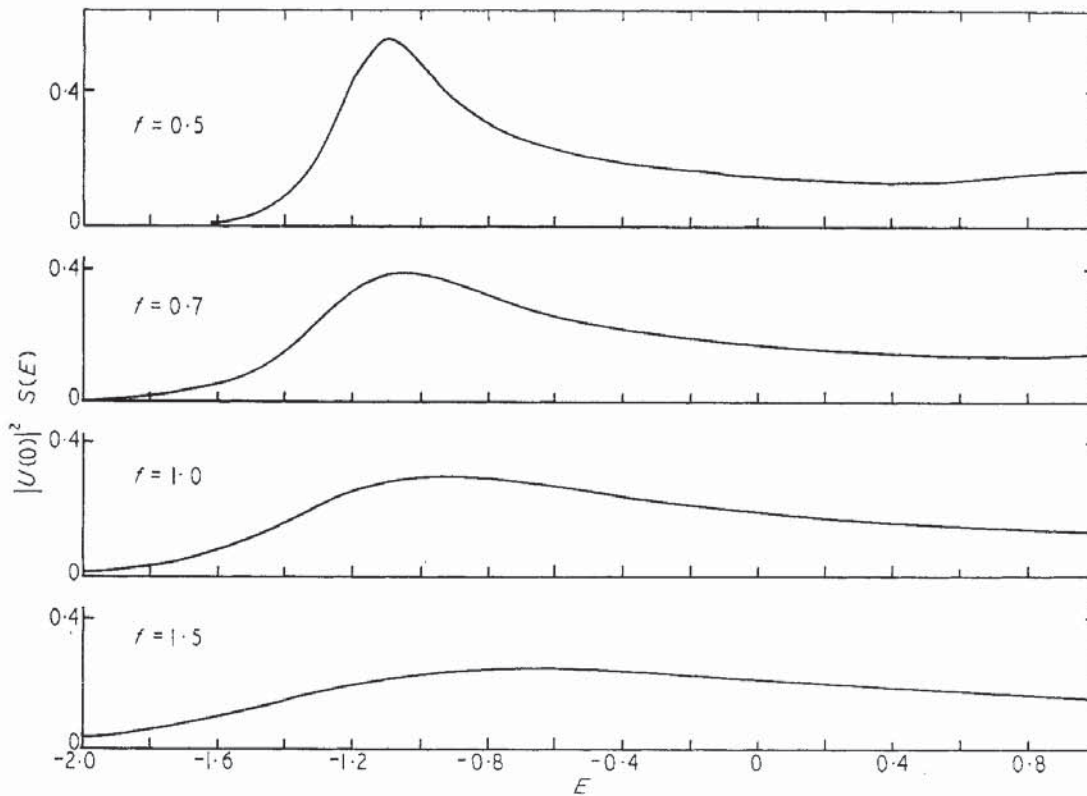
Figure 1(a).

Figure 1(b).

Figure 1(c).

Figure 1(d).

Figure 1. Plot of the function $\{A^2\pi^2 f^{1/2}\int_0^\infty (\chi_1{}^2/\xi)\, d\xi\}^{-1}$ of equation (16) for various values of the field strength parameter f. Energy measured relative to gap energy. Zero-field curve included for reference.

direction

$$\frac{\partial U}{\partial z}\bigg|_0 = (1-2t), \qquad m = 0 \tag{17a}$$

and the states with m unity have a slope only perpendicular to the z direction:

$$\frac{\partial U}{\partial x}\bigg|_0 = 1, \qquad |m| = 1. \tag{17b}$$

With equations (2b), (10), (15) and (17) this gives for the forbidden coefficient with the parallel and perpendicular polarization respectively

$$K_{F\parallel} = \frac{2\pi e^2 \hbar^2}{m^4 c \eta' \nu} \frac{|\langle c\mathbf{k}_0|\mathbf{M}|v\mathbf{k}_0\rangle|^2 (2t-1)^2}{A^2 \pi^2 f^{1/2} \int_0^\infty (\chi_1^2/\xi)\, d\xi} \tag{18a}$$

and

$$K_{F\perp} = \frac{2\pi e^2 \hbar^2}{m^4 c \eta' \nu} \frac{|\langle c\mathbf{k}_0|\mathbf{M}|v\mathbf{k}_0\rangle|^2}{A^2 \pi^2 f^{1/2} \int_0^\infty (\chi_1^2/\xi)\, d\xi}. \tag{18b}$$

3. Numerical integration

Equations (8) have been integrated numerically by Numerov's method using a device given by Cooley (1961) to obtain allowed values of the separation constant t. Because of the different position of t in equation (8a) from that of the energy Cooley's equation, (3.15)
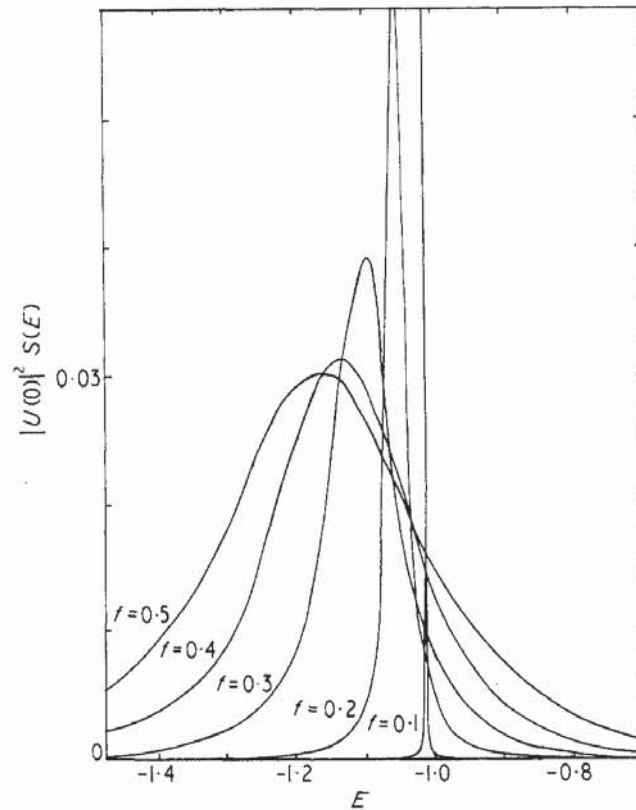

Figure 2. Plot of the function $(2t-1)^2/\{A^2\pi^2 f^{1/2}\int_0^\infty (\chi_1^2/\xi)\, d\xi\}$ of equation (18a) near the position of the 1s resonance for various values of field strength parameter f. Energy measured relative to gap energy. The oscillator strength is seen to grow as the field strength increases.

becomes

$$D(t) = \frac{(-Y_{m-1}+2Y_m-Y_{m+1})h^{-2}+U(t)P_m}{\sum\limits_{i=1}^{n} P_i^2/(ih)}. \tag{19}$$

The accuracy of the calculation was checked by working out some of the points to a much greater accuracy and the error was estimated to be about 2% or less, except for high energies ($> \frac{1}{2}$) and small fields ($< 0\cdot1$) for which it may have been as much as 5%. From the numerically evaluated solutions the quantities A^2 and $\int(\chi_1^2/\xi)\,d\xi$ were calculated and the absorption coefficients found by substituting into equations (16) and (18). The results of the calculations are shown in figures 1 and 2.

The time required to integrate the equations increased rapidly with decreasing field and it was found to be impracticable to obtain curves at fields so small that the forbidden absorption became interesting. A method of solving the equations by approximating the solutions by a polynomial may be more successful in those cases.

4. Discussion

For the allowed absorption curve at a field of $0\cdot06$ where the calculations start the 2s and 2p states are already very broad. A second-order perturbation calculation gives the energies of these lines as

$$E_2^{\pm} = -\tfrac{1}{4} \pm 3f - 42f^2 \tag{20}$$

and the peaks seen at $-0\cdot1$ and $-0\cdot37$ are presumably these. For larger fields the position of the 1s peak follows the second-order position of

$$E_1 = -1 - \frac{9f}{8} \tag{21}$$

fairly well until it reaches about $-1\cdot1$ where it remains until the field has increased to about $0\cdot5$ after which it again moves to higher energies and finally becomes so broad that it cannot be distinguished for E_1 greater than $0\cdot5$ which occurs for f about $1\cdot5$.

There are some marked differences between the results shown here and those obtained by Duke and Alferieff (1966) for a model potential. Compared with the present results, the curves of Duke and Alferieff show too little broadening, too little shift from the zero-field position and the wrong sign for the shift in the case of the 1s resonance.
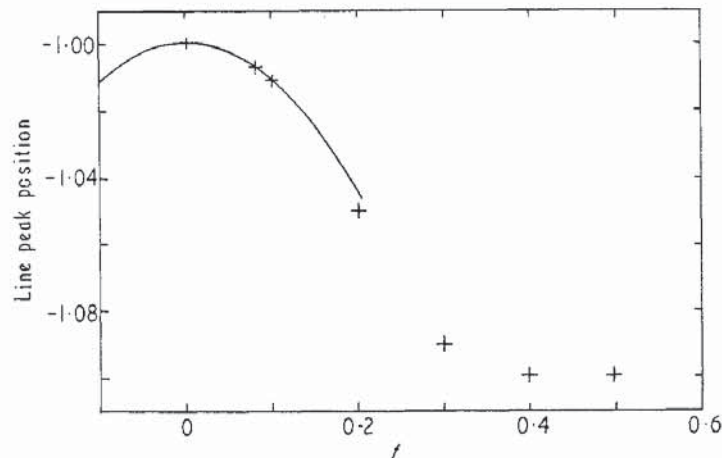

Figure 3. Plot of position of 1s resonance with field strength. Crosses mark position from numerical calculation; full line marks position from second-order perturbation theory.

The reduced broadening of the 1s resonance with their model potentials may be easily understood. Crudely, the resonance becomes broad when the potential barrier in the ζ

direction becomes as low as the energy of the 1s state. In the model potential the barrier is much larger than it should be. This presumably also partly accounts for the decrease in the shift of the line.

Little experimental work seems to have been done at fields so low that the excitonic effects are important. Vrehen (1966) has studied the effects of a small electric field and the
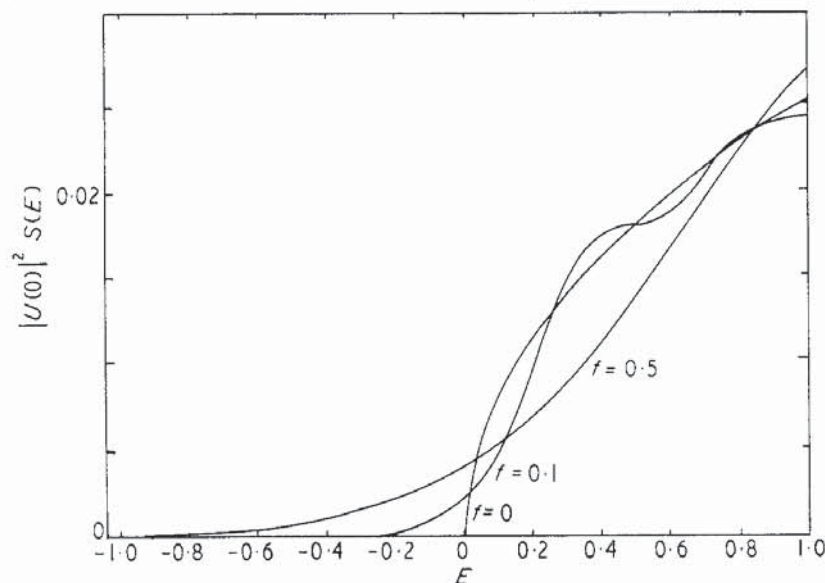

Figure 4. Allowed absorption curve in the absence of the Coulomb interaction for various field strengths. Scaling of ordinates corresponds to that of figures 1 and 2. Energy measured relative to gap energy.

absorption in germanium. If the broad peak at the band edge is assumed to be associated with the heavy hole giving a reduced mass of $0.036m$ then taking the dielectric constant of Ge to be 16 gives the exciton rydberg as 0.0019 ev and the exciton Bohr radius as 235 Å. The theoretical curves show that the peak should disappear for a field of about 1.5 rydbergs per Bohr radius or about 1200 v cm^{-1}. Vrehen's curves show the exciton disappearing at about 1000 v cm^{-1}. Considering that the elementary theory does not take into account the zero-field broadening, the complex form of the valence band or the central cell correction which are normally considered to be important the discrepancy is not significant.

Before the peak is extinguished Vrehen finds that it moves to higher energies as predicted by the theory.

Many experiments have been carried out using cuprous oxide in which forbidden absorption is seen. It is, therefore, rather unfortunate that it was not possible to analyse the forbidden case.

One interesting feature, however, does occur in the forbidden absorption at comparatively high fields when the light is polarized parallel to the field (figure 2). As the field increases the 1s state gets an admixture of the 2p state and therefore exhibits forbidden absorption. This is exactly analogous to an effect seen in cuprous oxide by Nikitine *et al.* (1962) who observed forbidden absorption by the s and d states in the presence of an electric field.

5. Conclusion

The available experimental evidence indicates that, when a crystal exhibits a good sharp exciton series, this theory may describe its behaviour in an electric field well though since the evidence is scanty it is hard to draw a firm conclusion. It would be very interesting to see the results of some more experiments on these materials.

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