PHYSICAL REVIEW B VOLUME 13, NUMBER 4 15 FEBRUARY 1976

Inhomogeneous broadening of the Lyman-series absorption of simple hydrogenic donors*

David M. Larsen
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

(Received 6 October 1975)

Inhomogeneous broadening of hydrogenic-donor $1s$-np transitions due to the electric fields and field gradients of randomly distributed donor and acceptor ions is considered for the case of a simple isotropic parabolic conduction band. It is shown that for n even, the transition has a nearly unshifted and relatively sharp central line, whereas for n odd, the central peak is missing; what remain are peaks symmetrically split about the unperturbed transition energy and strongly broadened. Detailed calculations are made for the $1s$-$2p$ and $1s$-$3p$ line shapes. These line shapes are in qualitative but not quantitative agreement with experimental spectra for GaAs; it is pointed out, however, that the theory is self-consistent only for ionized impurity concentrations well below 4×10^{13} cm^{-3}, characteristic of the purest GaAs samples studied to date. The self-consistency of the broadening theory for donors in strong magnetic fields is discussed.

I. INTRODUCTION

Quantitative studies of magneto-optical line shapes of shallow donors in high-purity epitaxial n-GaAs have shown that the observed broadening is due to electric fields and electric field gradients arising from fixed charged impurities located at more-or-less randomly scattered sites in the host crystal.[1,2] It is expected that this broadening mechanism should be important also in other semiconductor materials of high purity which contain residual compensating impurities.

The principles underlying the usual picture of inhomogeneous broadening of neutral-donor transitions from random electric fields and field gradients are straightforward. One assumes that the transition linewidth from each individual donor is field independent (one often further assumes that the natural line shape can be approximated by a δ function, because inhomogeneous widths are frequently orders of magnitude larger than natural linewidths). The electric fields and their gradients serve only to shift the energies and oscillator strengths of the donor transitions. Since optical-absorption experiments record the sum of the absorptions of very many donors, each with a slightly different energy and oscillator strength, the observed line has a shape determined in large part by the statistical distribution of electric fields and field gradients at the neutral donors. Omitting second and higher derivatives of the electric field from the theory is justifiable when the fixed ions producing the fields are at sufficiently large distances from the neutral donors (i.e., distances much larger than the characteristic dimensions of the initial and final states of the donor).

It is well known that a hydrogenic atom in a uniform electric field has a finite lifetime against electron emission which decreases rapidly with increasing electric field (and therefore that the hydrogenic levels experience broadening which very rapidly increases with electric field strength). It follows that a necessary condition for self-consistency of the model of inhomogeneous broadening described above (we shall refer to this henceforth as the "simple inhomogeneous broadening theory" or SIBT) is that for a large majority of neutral donors the electric fields at the donor centers are sufficiently weak that the lifetime broadening due to the possibility of dissociation of the donor in either the initial or final state of the optical transition is small compared to the inhomogeneous broadening.

In this paper we develop a SIBT for the case of $1s$ to p state transitions of simple hydrogenic donors at low temperatures in semiconductors having a simple, spherical, parabolic conduction band. Assuming that the fixed ions giving rise to the broadening fields are randomly distributed, we estimate the maximum ion concentrations for which a SIBT is self-consistent. We find that the maximum ionic concentration allowed for a self-consistent treatment of the $1s \rightarrow 2p$ transitions in GaAs is almost an order of magnitude smaller than ion concentrations in the purest samples for which donor spectroscopy has been reported. As might therefore be expected, our calculated line shapes do not agree quantitatively with experimental line shapes.

For odd n we find that $1s \rightarrow np$ transitions can not occur to levels with zero linear Stark splitting. Therefore the predicted transition lines are split and strongly broadened, whereas for n even the lines are relatively sharp and nearly unshifted.

We have previously applied a SIBT to GaAs donor transitions in moderately strong magnetic fields.[1,2] It was found possible in some cases to achieve very good quantitative fits to the line shapes near the line peaks[2] in the same samples for which we now find the zero-field calculations to fail. A possible explanation for this fact will be advanced.

Line-shape calculations for the $1s \rightarrow 2p$ and $1s \rightarrow 3p$ transitions will be presented for ion concentrations in which our criterion for self-consistency is satisfied. These calculations give insight into the striking qualitative differences between the $1s \rightarrow 2p$ and $1s \rightarrow 3p$ line shapes observed.

II. ELECTRIC FIELD BROADENING

We begin by considering broadening due to the Stark effect. It turns out that most of the important qualitative features of the donor transition line shapes can be inferred from considerations of electric field broadening alone.

Our discussion is based on the effective-mass Hamiltonian H of a single neutral hydrogenic donor perturbed by the fixed scattered point ions

$$H = H_0 - e\,V_{\text{ext}}(r)\,, \qquad H_0 = p^2/2m^* - e^2/\epsilon_0 r\,, \tag{1}$$

where ϵ_0 is the static dielectric constant, e is the magnitude of the electron charge, and V_{ext} is the potential due to the surrounding donor and acceptor ions. Defining the charge and position of the jth ion by e_j $(e_j = \pm e)$ and $\vec{\mathrm{R}}_j$, respectively, V_{ext} can be written

$$V_{\text{ext}} = \sum_j \frac{e_j}{\epsilon_0 |\vec{\mathrm{R}}_j - \vec{\mathrm{r}}|} = \frac{1}{2} \sum_j \frac{e_j}{\epsilon_0 R_j} \sum_{k=0}^{\infty} \sum_{m=0}^{k} \bar{\epsilon}_m \frac{(k-m)!}{(k+m)!} \times P_k^m(\cos\theta_0)\,[e^{im\varphi_0} P_k^m(\cos\theta_j)\, e^{-im\varphi_j} + \text{c.c.}\,] \times \left(\frac{r}{R_j}\right)^k, \tag{2}$$

where $\bar{\epsilon}_m = 2$ except at $m = 0$ for which $\bar{\epsilon}_0 = 1$, R_j, Θ_j, and φ_j are the spherical coordinates of the jth ion and r, Θ_0, and φ_0 are those of the donor electron. The multipole expansion of (2), discussed in Ref. 1, is most useful when the size of the donor atom in the excited states of interest is small compared to any R_j. In that circumstance the expansion can be truncated at some low value of k and the perturbed energy levels of (1) can readily be evaluated as functions of the R_j's.

The lowest nontrivial approximation to V_{ext} is obtained by neglecting all terms in (2) with $k > 1$. (The $k = 0$ term simply shifts the zero of energy for a given neutral donor, and we shall neglect it henceforth.) In this approximation we have $V_{\text{ext}} \cong (\vec{\mathrm{F}}/e) \cdot \vec{\mathrm{r}}$ where $\vec{\mathrm{F}}/e = \sum e_j \vec{\mathrm{R}}_j / \epsilon_0 R_j^3$ is the electric field of ions evaluated at $r = 0$, and H in (1) becomes the Hamiltonian for a hydrogenic atom in a uniform electric field. For weak electric fields the general formula for bound-state energy levels with quantum numbers n, m, n_1, and n_2 is[3]

$$R\left[-\frac{1}{n^2} + 3\frac{Fa_0}{2R}\, n(n_1 - n_2) - \left(\frac{Fa_0}{2R}\right)^2 \frac{n^4}{8} \times [17n^2 - 3(n_1 - n_2) - 9m^2 + 19] + O\left((Fa_0/R)^3\right)\right], \tag{3}$$

where n is the principal quantum number and m is the quantum number for the component of orbital angular momentum along the electric field direction; a_0 and R are the effective Bohr radius and Rydberg of the hydrogenic donor, and n_1 and n_2 are integers greater than or equal to zero which obey

$$n = n_1 + n_2 + |m| + 1\,. \tag{4}$$

To calculate the inhomogeneous broadening of, say, the $1s \rightarrow 2p$ transition in the SIBT, one calculates the position and oscillator strength of each of the four excited levels[4] in the electric field using (3) and the zero-order wave functions ψ_{n,m,n_1,n_2} given by

$$\begin{aligned} \psi_{2,0,1,0} &= (1/\sqrt{2})(\varphi_{2s} - \varphi_{2p_0}) \\ &\qquad \text{(shift linear in } F = 3Fa_0)\,, \\ \psi_{2,0,0,1} &= (1/\sqrt{2})(\varphi_{2s} + \varphi_{2p_0}) \\ &\qquad \text{(shift linear in } F = -\,3Fa_0)\,, \\ \psi_{2,\pm 1,0,0} &= \varphi_{2p_{\pm 1}} \quad \text{(shift linear in } F = 0)\,, \end{aligned} \tag{5}$$

where the φ's are the familiar simultaneous eigenfunctions of H_0 and total orbital angular momentum. One then calculates the inhomogeneous line profile by weighting each transition energy jointly (i) by the probability that the electric field has the proper strength to shift one or more of the states (5) to the required energy and, (ii) by the oscillator strength of the transition to each of the states so shifted. In order to carry out such a calculation one needs a probability distribution $p(\mathcal{E})$ for the electric field strength. We approximate this by assuming that the impurity ions are randomly distributed, in which case, as is well known, $p(\mathcal{E})$ is given by

$$p(\mathcal{E}) = \frac{2}{\pi}\, \mathcal{E} \int_0^{\infty} dx\, x\, e^{-\beta x^{3/2}} \sin \mathcal{E} x\,, \tag{6}$$

where $\mathcal{E}$ is the electric field in units of $e n_I^{2/3}/\epsilon_0$, with n_I the total ionized impurity concentration, and[5] $\beta = \frac{4}{15}(2\pi)^{3/2}$. In Fig. 1 we show a plot of $p(\mathcal{E})$.

We have already pointed out that the SIBT is self-consistent only for electric fields which are not too strong. To estimate how large the field can be we note that the $n = 2$ linewidth grows extremely rapidly with electric field strength so that we can define a critical field F_{crit}/e such that for practical purposes the contribution to the line shape from donors experiencing fields greater than F_{crit}/e is not properly given by the SIBT whereas those donors in fields below the critical field are well described by this model.

Of course there is some arbitrariness in choosing F_{crit}, but because of the extreme sensitivity of the linewidth to the electric field strength we are safe in bracketing F_{crit} according to

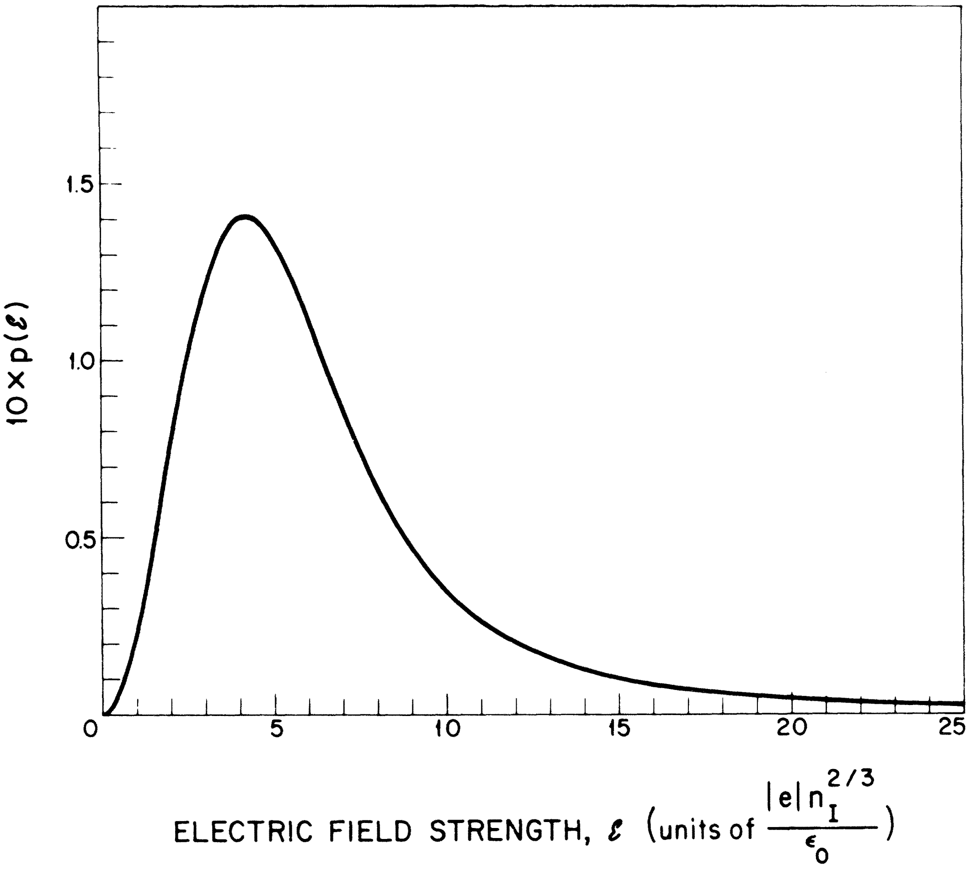

FIG. 1. Probability distribution of the strength of the electric field produced by randomly scattered point charges with number density n_I and evaluated at a randomly chosen point. (This is the Holtzmark distribution.)

$$0.005 < \frac{F_{\rm crit}\, a_0}{R} < 0.02$$

for the $n=2$ levels.[6,7] In fact, a reasonable choice of $F_{\rm crit}$, and the one which we shall use, is

$$F_{\rm crit}\, a_0/R = 0.01 \quad (n=2 \text{ levels}). \qquad (7)$$

For us to be confident that the SIBT may well describe the electric-field-induced inhomogeneous broadening we must demand that a large fraction of the neutral donors see electric fields smaller than $F_{\rm crit}/e$. If we take that fraction to be, say $\frac{9}{10}$, then solving

$$\int_0^{\mathcal{E}_{\rm crit}} p(\mathcal{E}) = 0.9,$$

we find $\mathcal{E}_{\rm crit} \cong 14$. Identifying $(e^2 n_I^{2/3}/\epsilon_0)\,\mathcal{E}_{\rm crit} = F_{\rm crit}$ and inserting into (7) yields $n_I a_0^3 \cong 0.7\times 10^{-5}$; hence the criterion

$$n_I a_0^3 \lesssim 0.7\times 10^{-5} \quad (n=2\text{ levels}). \qquad (8)$$

This formula gives, in effect, an estimate of the maximum ionized impurity concentration at which the inhomogeneous broadening calculation of the $n=2$ levels can be expected to be self-consistent when no magnetic field is present.[8] We know of no published data on shallow donor spectra of III-V semiconductors in which n_I is small enough to satisfy (8).

Berman[9] and coworkers have attempted to apply a calculation of inhomogeneous broadening of the type described here to the $1s \rightarrow 2p$ transition line shape in shallow GaAs donors for $n_I a_0^3 \sim 1.0\times 10^{-4}$, an order of magnitude higher than (8). (In GaAs, $a_0 = 10^{-6}$ cm.) Those authors neglect terms quadratic in F in (3) for the states $\psi_{2,0,1,0}$ and $\psi_{2,0,0,1}$ and all terms in (2) with $k>1$. We show in Sec. III that certain field gradient ($k=2$) terms play a very important role in determining the line shape, especially at ionized impurity concentrations obeying (8). The line shapes obtained in Ref. 9 are not in quantitative agreement with experiment.[10]

Returning to our line-shape calculation we observe from (5) that two levels are strongly shifted by the electric field due to the linear Stark effect. To obtain an expression for the Stark shifts in terms of $\mathcal{E}$ we write first F in terms of $\mathcal{E}$:

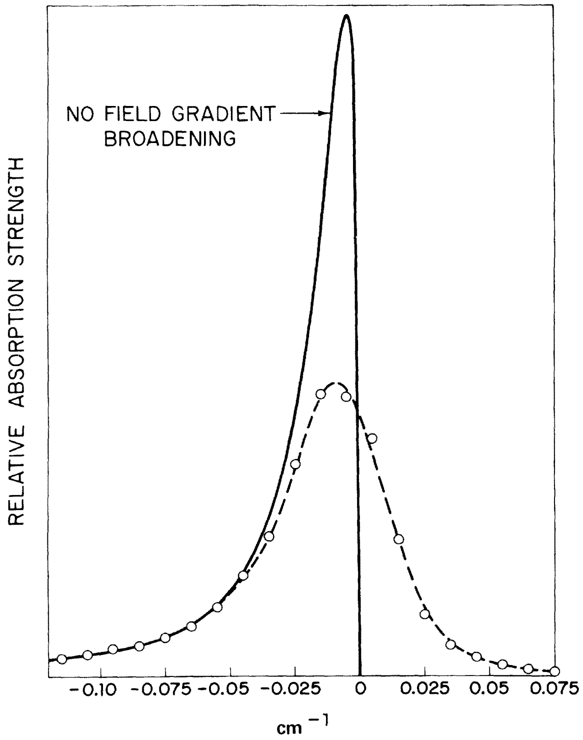

FIG. 2. Calculated absorption line shape of the central peak of the GaAs $1s$-$2p$ transition. The solid curve includes only quadratic Stark-effect broadening. The dashed curve includes the combined Stark and correlated field gradient broadening; it was calculated by the Monte Carlo technique using 8000 random configurations of point charges. For this calculation we have taken $n_I a_0^3 = 0.5\times10^{-5}$.

$$F=(e^2/\epsilon_0)n_I^{2/3}\mathcal{E}=(2R/a_0)(n_I a_0^3)^{2/3}\mathcal{E}\,, \tag{9}$$

where we have used $R=e^2/2\epsilon_0 a_0$. The linear Stark shift of the $n=2$ levels is then

$$\pm 6R(n_I a_0^3)^{2/3}\mathcal{E}\,. \tag{10}$$

This is to be compared to the quadratic Stark shift of the $2p_{\pm1}$ levels, which have no linear Stark shift, of

$$-156R(n_I a_0^3)^{4/3}\mathcal{E}^2\,. \tag{11}$$

From the smallness of (11) relative to (10) in the range of most probable $\mathcal{E}$ values we can immediately guess that the line shape will consist of a sharp central spike with two relatively broad wings of low amplitude, when (8) is satisfied by n_I.

If we imagine an absorption experiment in which an incident plane polarized beam is employed we can see easily from the fact that electric fields from random charge distributions are isotropic, that the average oscillator strength for each of the levels in (5) is proportional to the square of the amplitude of their p wave-function admixture.[11] Thus the central level has, on average, $\frac{2}{3}$ of the total $1s\rightarrow 2p$ oscillator strength.

We have used $p(\mathcal{E})$ from (6) and the line shift given by (11) to calculate the shape of the sharp central peak, labeled "no field gradient broadening" in Fig. 2. The peak absorption strength of the central line is approximately three orders of magnitude greater than that of the wing absorption lines contributed by states split by the linear Stark effect (neglecting the additional quadratic shift in these states) for $n_I a_0^3 = 0.5\times10^{-5}$. This disparity between peak absorption strengths increases with decreasing n_I so that the wings, for most purposes, can be neglected when (8) is satisfied.

We shall see in Sec. III that the field gradient terms in (2) neglected so far, contribute line shifts of order $n_I a_0^3$ for small n_I. From (10) it would appear, therefore, that these terms can be expected to have little effect on the shape of the wings; they should, however, play an important role in determining the shape of the central peak since, from (11), electric-field-induced shifts are of order $(n_I a_0^3)^{4/3}$.

Before leaving the subject of electric field broadening, we examine the line shape expected for the $1s\rightarrow 3p$ transition, which turns out to be qualitatively different from the $1s\rightarrow 2p$ line shape.

We have just pointed out that the dominant feature of the $1s\rightarrow 2p$ transition line is the sharp central peak arising from the very weakly shifted degenerate $2p_{+1}$ and $2p_{-1}$ levels. It is not hard to see that no analogue of this peak exists for $1s\rightarrow 3p$. The reason is that the electric field couples the $3p_{+1}$ and $3p_{-1}$ levels to $3d_{+1}$ and $3d_{-1}$ levels, respectively; all four of these levels are degenerate in the absence of an electric field. The resulting mixed P and D states have a linear Stark splitting of

$$\pm 9R(n_I a_0^3)^{2/3}\mathcal{E}\,. \tag{12}$$

To obtain a sharp central line we must look for transitions to states with zero linear Stark shift. Examination of (3) and (4) shows that $n=3$ states do exist with zero linear Stark shift. These are characterized by $m=\pm2$, $n_1=n_2=0$ and $m=0$, $n_1=n_2=1$. Dipole transitions from the $1s$ state to states with $|m|\geq 2$ are forbidden in general by angular momentum conservation. Thus we must investigate the remaining state ($m=0$, $n_1=n_2=1$) to see if it has a nonzero oscillator strength for transitions from the $1s$ level. Since this oscillator strength can come only from admixture of $3p_0$ level, we inquire whether any $3p_0$ admixture is present in the $m=0$, $n_1=n_2=1$ level.

To answer this question we write down the most general $m=0$ $n=3$ wave function in the form $\psi_0 = a_1\varphi_{3s}+a_2\varphi_{3p0}+a_3\varphi_{3d0}$ and require zero linear Stark shift by setting

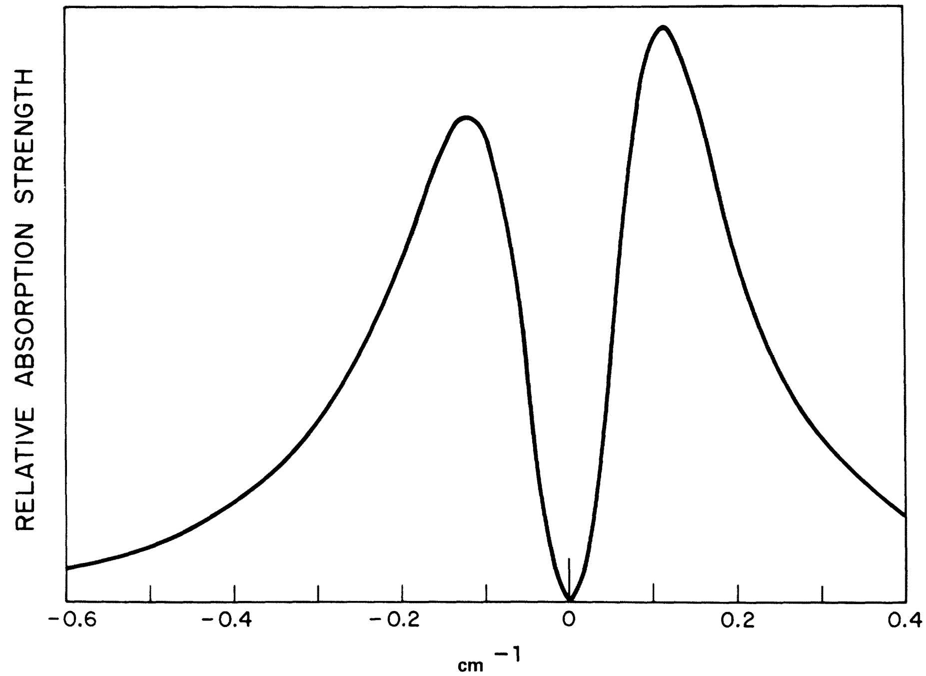

FIG. 3. Calculated absorption line shape of the $1s$-$3p$ transition in GaAs considering linear and quadratic Stark-effect broadening but neglecting field gradient broadening. For this calculation we have taken $n_I a_0^3 = 0.05\times10^{-5}$. The unshifted $1s\rightarrow 3p$ transition occurs at 0 cm^{-1}.

$$\langle\varphi_j|\,(H_0 - Fz)\,|\,\psi_0\rangle = -\tfrac{1}{9}R\,\langle\varphi_j|\,\psi_0\rangle\,, \tag{13}$$

where j stands for $3s$, $3p_0$, or $3d_0$. In this way we find that the state $\psi_{3,0,1,1}$ is a mixture of $3s$ and $3d_0$ levels and therefore has no dipole oscillator strength from the $1s$ level.

For completeness we list the $n=3$ levels and their linear Stark shifts S_L:

$$\begin{aligned}
\psi_{3,0,1,1} &= (1/\sqrt{3})\,(-\varphi_{3s} + \sqrt{2}\,\varphi_{3d_0}), && S_L = 0\,,\\
\psi_{3,0,2,0} &= (1/\sqrt{3})\,[\varphi_{3s} + (\tfrac{3}{2})^{1/2}\,\varphi_{3p_0} + (1/\sqrt{2})\,\varphi_{3d_0}], &&\\
& && S_L = 9Fa_0\,,\\
\psi_{3,0,0,2} &= (1/\sqrt{3})\,[-\varphi_{3s} + (\tfrac{3}{2})^{1/2}\,\varphi_{3p_0} - (1/\sqrt{2})\,\varphi_{3d_0}], &&\\
& && S_L = -9Fa_0\,,\\
\psi_{3,\pm1,1,0} &= (1/\sqrt{2})\,(\varphi_{3p_{\pm1}} + \varphi_{3d_{\pm1}})\,, && S_L = \tfrac{9}{2}Fa_0\,,\\
\psi_{3,\pm1,0,1} &= (1/\sqrt{2})\,(\varphi_{3p_{\pm1}} - \varphi_{3d_{\pm1}})\,, && S_L = -\tfrac{9}{2}Fa_0\,,\\
\psi_{3,\pm2,0,0} &= \varphi_{3d_{\pm2}}\,, && S_L = 0\,.
\end{aligned} \tag{14}$$

These equations are the $n=3$ analogues of Eq. (5). Substantial lifetime broadening of the $n=3$ levels occurs at fields at which the $n=2$ level is still sharp; we estimate[6]

$$F_{\mathrm{crit}}\,a_0/R = 0.0025 \quad (n=3 \text{ levels})\,,$$

which, setting $\mathcal{E}_{\mathrm{crit}} = 14$ as before and using (9), gives

$$n_I a_0^3 \lesssim 0.8\times10^{-6} \quad (n=3 \text{ levels}) \tag{15}$$

as a self-consistency requirement for the $n=3$ calculation analogous to Eq. (8). In Fig. 3 we show the predicted $3p$ line shape at $n_I a_0^3 = 0.05\times10^{-5}$ assuming electric field broadening only. (Field gradient broadening produces a negligible effect on the $3p$ line shape.) Notice that the absorption peaks are nearly symmetrical with respect to the unperturbed position of the $1s\rightarrow 3p$ transition. Qualitatively speaking, the $1s\rightarrow 3p$ transition differs from the $1s\rightarrow 2p$ transition in that the sharp central line near the unperturbed transition energy is missing.

Study of Eqs. (3) and (4) suggests that a sharp central peak is missing for *all* $1s\rightarrow np$ transitions in which n is odd and is present for transitions in which n is even (always assuming, of course, that n_I is small enough that a SIBT approach is valid). For n even there always exist $|m| = 1$ states with $n_1 = n_2$. Such states, having zero linear Stark shift, will give a sharp central line if there is a nonzero oscillator strength to them from $1s$. It is easy to show that these states have odd parity; therefore one expects a nonvanishing oscillator strength in the transition from $1s$. On the other hand, for n odd and $|m| = 0$ or 1 there is only a single state with zero linear Stark shift (it has quantum numbers $n_1 = n_2 = \frac{1}{2}(n-1)$ and $|m| = 0$). One can show that this is a state of even parity[12]; it cannot, therefore, be reached by a dipole transition from the $1s$ level, and no sharp central line is present.

III. FIELD GRADIENT BROADENING

We now consider contributions of the $k=2$ terms in (2) to the shifts of the Stark-split levels. In general, these shifts are of order $(n_I a_0^3)R$ which means that they are smaller than the linear Stark shifts [of order $(n_I a_0^3)^{2/3} R$] but larger than the quadratic shifts [of order $(n_I a_0^3)^{4/3} R$] in the limit $n_I \to 0$. Thus at low impurity ion concentrations the $k=2$ terms should play an important role in the broadening of the central sharp peaks associated with the $1s \to np$ transitions for n even, but they should not strongly affect the relatively broad lines arising from the linear Stark shift.

Recall that the sharp peaks are associated with doubly degenerate odd parity states with $m = \pm 1$. For the $1s \to 2p$ transition, for which we will make explicit calculations, the central peak is associated with transitions to the levels [see (5)].

$$\varphi_{2p_{\pm 1}} = \frac{1}{8(\pi a_0^5)^{1/2}} e^{\pm i\varphi} \sin\theta\, r\, e^{-r/2a_0} . \qquad (16)$$

Treating the field gradient terms of (2) in lowest-order perturbation theory we find that the $m=0$ term has in general a nonzero expectation value in the states $\psi_{n,\pm 1,(n/2)-1,(n/2)-1}$ but does not break the degeneracy of these levels. Effects due to the $m=0$ term in the broadening of donor magneto-optical spectra have been discussed in some detail in Ref. 1. The shift induced by this term is simply the classical energy shift arising from the interaction of the electric field gradient produced by the surrounding ions with the quadrupole moment of the charge distribution of the electron bound to the neutral donor. This shift is given by

$$\tfrac{1}{4} eQ \frac{\partial \mathcal{E}_z}{\partial z} , \qquad (17)$$

where z here refers to the axis of symmetry of the wave functions $\psi_{n,\pm 1,n/2-1,n/2-1}$; this axis lies along the electric field direction. The quadrupole moment Q in (17) is defined in the usual way

$$Q = \langle \psi_{n,\pm 1,n/2-1,n/2-1} | (3z^2 - r^2) | \psi_{n,\pm 1,n/2-1,n/2-1} \rangle , \qquad (18)$$

and the field gradient at the donor center is given by

$$\frac{\partial \mathcal{E}_z}{\partial z} = -\sum \frac{e_j}{\epsilon_0 R_j^5} (3Z_j^2 - R_j^2), \qquad (19)$$

where Z_j is the component of $\vec{R}_j$ along the direction of the electric field produced at the donor center by the same ions summed over in (19). We point out here that the statistical distribution of the gradient $\partial \mathcal{E}_z / \partial z$ defined in (19) from an ensemble of impurity ions located at random positions in the semiconductor is not identical to the well-known Lorentzian distribution derived for this quantity for the case in which the z direction is fixed in a direction independent of the positions and charges of the impurity ions.[1] Thus the field gradient distribution of interest to us here is correlated with the electric field. We shall henceforth refer to such field gradient distributions as "correlated" distributions to distinguish them from the usual "uncorrelated" distributions of previous literature.

We will neglect in general the effect of the $k=2$ $m=1$ term on the sharp central line because for n even this term connects states with zero linear Stark shift only to states with nonzero shift. Thus, for example, this term for $n=2$ connects the $2p_{\pm 1}$ states to the symmetrically split levels $\psi_{2,0,1,0}$ and $\psi_{2,0,0,1}$ of Eq. (5). The resulting shift of the $2p_{\pm 1}$ levels is of higher order than $(n_I a^3)^{4/3}$ and can be neglected.

On the other hand the $k=2$, $m=2$ term in (2) turns out to be very important; it breaks the degeneracy of the $m = \pm 1$ states with zero linear Stark shift. This term does not appear to have been discussed previously in the literature, so it would seem worthwhile to look at its effects in some detail here.

From (2) the $k=m=2$ term T_{22} can be written

$$T_{22} = \tfrac{3}{8} [(T_A - iT_B) e^{2i\varphi_0} + (T_A + iT_B) e^{-2i\varphi_0}] \rho^2 , \qquad (20)$$

where

$$\begin{aligned} T_A &= \frac{1}{3} \sum \frac{e_j}{\epsilon_0 R_j^3} P_2^2(\cos\Theta_j) \cos 2\varphi_j \\ &= \sum \frac{e_j}{\epsilon_0 R_j^5} (X_j^2 - Y_j^2), \\ T_B &= \frac{1}{3} \sum \frac{e_j}{\epsilon_0 R_j^3} P_2^2(\cos\Theta_j) \sin 2\varphi_j \\ &= 2 \sum \frac{e_j}{\epsilon_0 R_j^5} (X_j Y_j), \end{aligned} \qquad (21)$$

and we have used $r^2 P_2^2(\cos\Theta_0) = 3\rho^2$ and $R_j^2 = X_j^2 + Y_j^2 + Z_j^2$.

The splitting induced by T_{22} in the $2p_{\pm 1}$ levels is found by solving the secular determinant

$$\begin{vmatrix} E_0 - \lambda & 9ea_0^2(T_A - iT_B) \\ 9ea_0^2(T_A + iT_B) & E_0 - \lambda \end{vmatrix} = 0,$$

where we have used $\langle \varphi_{2p\pm 1} | \rho^2 e^{\pm 2i\varphi} | \varphi_{2p\mp 1} \rangle = \langle \varphi_{2p\pm 1} | \rho^2 | \varphi_{2p\pm 1} \rangle = 24 a_0^2$ and E_0 is the energy of the $2p_{\pm 1}$ levels when $T_{22} = 0$. The energy shift is

$$E_0 - \lambda = \pm 9 (T_A^2 + T_B^2)^{1/2} e a_0^2 . \qquad (22)$$

The uncorrelated statistical distribution of $(T_A^2 + T_B^2)^{1/2}$ from random spatial distributions of ions can be shown to be given by

$$P[(T_A^2 + T_B^2)^{1/2}] = \gamma (T_A^2 + T_B^2)^{1/2} / (T_A^2 + T_B^2 + \gamma^2)^{3/2} ,$$
$$\gamma = \tfrac{8}{9} \pi (e/\epsilon_0) n_I . \qquad (23)$$

Although the result given in (23) is of interest in its own right, our present purposes require calculation of the correlated distribution of $(T_A^2 + T_B^2)^{1/2}$. For this, as for all correlated distributions, we must resort to Monte Carlo methods.

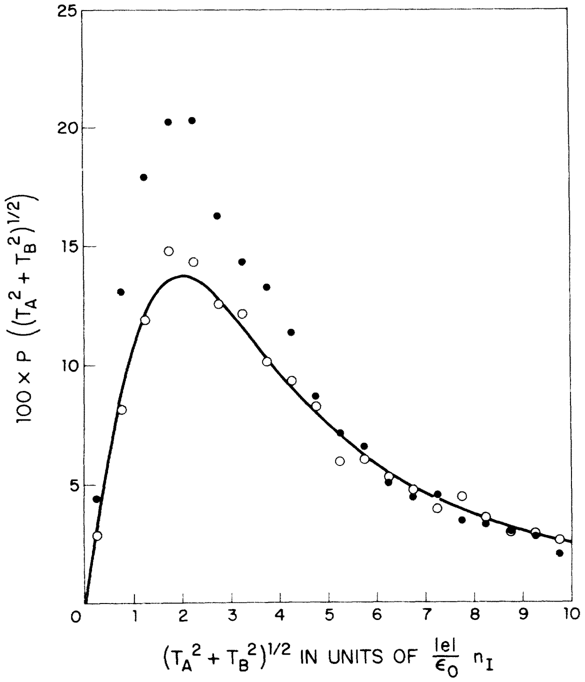

FIG. 4. Comparisons of the exact uncorrelated distribution of $(T_A^2+T_B^2)^{1/2}$ (solid curve) with the Monte Carlo calculation (open circles) and with the Monte Carlo calculation of the correlated distribution of the same quantity (solid circles). 8000 random configurations of point charges are used.

Our procedure is to simulate an ensemble of neutral donors acted on by fields and/or field gradients of an infinite number of charged ions of density n_I by randomly scattering 50 positive and 50 negative ions in a sphere of radius $(300/4\pi n_I)^{1/3}$ around each donor in the ensemble. The electric field at the center of the sphere is calculated first and then T_A, T_B, and $\partial\mathcal{E}_z/\partial z$ are calculated from (21) and (19) using the electric field direction as the z axis (when correlated distributions are desired). A more detailed discussion of the Monte Carlo method is given in Ref. 1.

In Fig. 4 we compare the correlated distribution of $(T_A^2+T_B^2)^{1/2}$ with the corresponding uncorrelated distribution calculated two ways: (i) by the Monte Carlo technique and (ii) using (23). We notice that the Monte Carlo approximation is reasonably good for the uncorrelated distribution; we have no reason to think that it should be markedly less accurate for the correlated distribution. Notice that the correlated distribution tends to favor small values of $(T_A^2+T_B^2)^{1/2}$ relative to the uncorrelated distribution.[13,14] From (17), (22), and the fact that for the $2p_{\pm1}$ states $Q=-12a_0^2$ we conclude that the total field-gradient-induced shift of the $2p_{\pm1}$ levels is proportional to

$$-\frac{\partial\mathcal{E}_z}{\partial z} \pm 3(T_A^2+T_B^2)^{1/2}\,. \qquad (24)$$

Monte Carlo calculations of the correlated and uncorrelated distributions of this quantity are shown in Fig. 5. Both distributions appear to have a "dimple" in the middle (although this is less well established for the correlated distribution) and the line shapes appear to be more than three times broader than those we would have calculated using only $-\partial\mathcal{E}_z/\partial z$ in (24).

Our final line shape for the sharp central line of the $1s\rightarrow 2p$ transition is obtained from combining the field gradient shifts proportional to (24) with the quadratic Stark shift of (11) to obtain for the total shift of the line the expression

$$(n_I a_0^3)\left(-6\frac{\partial\mathcal{E}_z}{\partial z} \pm 18(T_A^2+T_B^2)^{1/2} - 156(n_I a_0^3)^{1/3}\mathcal{E}^2\right)R\,. \qquad (25)$$

The correlated statistical distribution of this quan-

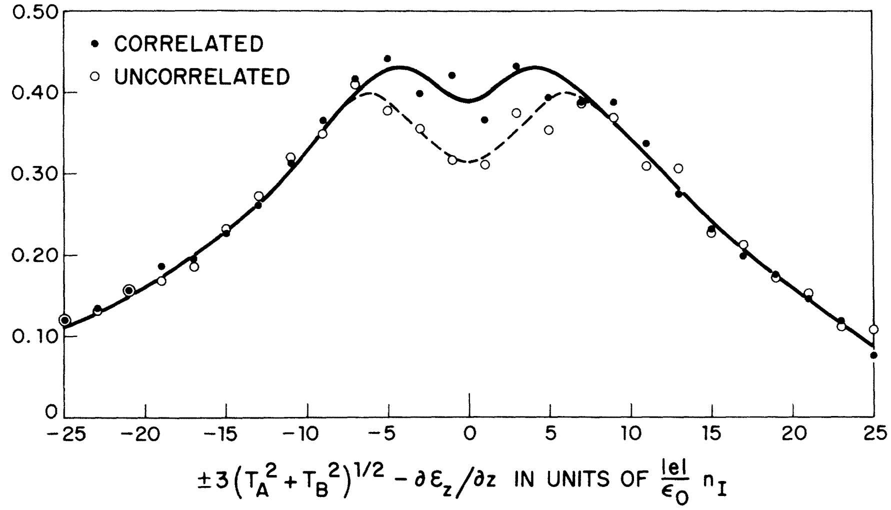

FIG. 5. Comparison of correlated (solid circles) and uncorrelated (open circles) distributions of $\pm 3\,(T_A^2+T_B^2)^{1/2}-\partial\mathcal{E}_z/\partial z$ calculated by the Monte Carlo method with 8000 random configurations of point charges. The curves serve merely as guides to the eye.

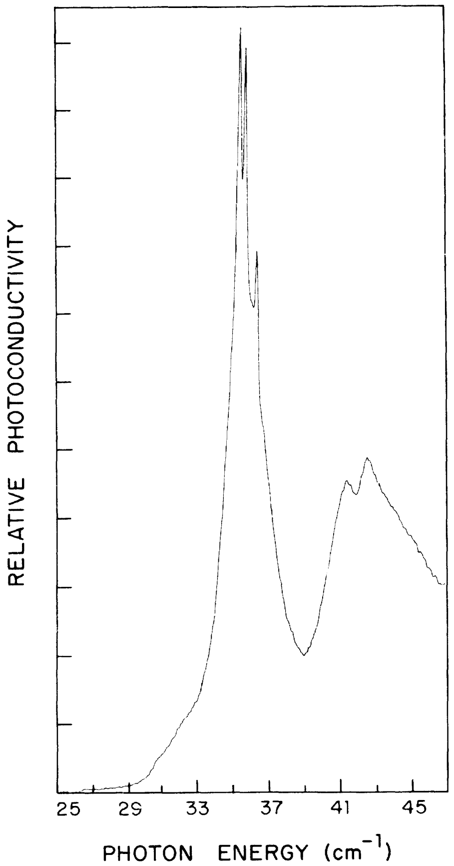

FIG. 6. Experimental zero-field photoconductivity spectrum of a high-purity GaAs sample at $T=1.57°$ with instrumental resolution of ~ 0.07 cm^{-1}.

tity for GaAs ($R=46.15$ cm^{-1}) is plotted in Fig. 2 for $n_I a_0^3 = 0.5\times 10^{-5}$, where it is compared to the quadratic Stark effect line shape, obtained neglecting all $k=2$ terms. It is clear that the field gradients play an important role in the $1s\rightarrow 2p$ transition line shape when (8) is satisfied.

IV. COMPARISON WITH EXPERIMENT

In Fig. 6 we show the low temperature ($T=1.57$ K) photoconductivity spectrum of an epitaxial GaAs crystal[15] for which electrical measurements indicate $n_A = 2\times 10^{13}$ cm^{-3} (hence $n_I a_0^3 = 4\times 10^{-5}$), $n_D = 5\times 10^{13}$ cm^{-3}, and $\mu_{77°} = 210\,000$ cm^2/V sec. The three peaks on the sharp strong line near 35 cm^{-1} are $1s\rightarrow 2p$ transitions from different donor species. Their splitting is due to small differences in chemical shifts among the various species of residual donors in the sample.[16] A second, broader line with two peaks appears to the right of the $1s\rightarrow 2p$ line. The calculated unperturbed $1s\rightarrow 3p$ transitions for the two strongest donors lie near 42 cm^{-1}, between the two peaks of the broader line. We tentatively identify the double peaked structure as the $1s\rightarrow 3p$ Stark split lines (see Fig. 3).

Although the purity of the sample whose spectrum is shown in Fig. 6 is close to the present state of the art for GaAs, its zero-temperature ionized impurity concentration far exceeds the limit set by either (8) or (15). It would be surprising if our SIBT could achieve a quantitative fit to either the $1s\rightarrow 2p$ or $1s\rightarrow 3p$ transition line shape; in fact we cannot properly fit these lines. Nevertheless our theory does account for certain qualitative features of the line shapes.

In particular, the $1s\rightarrow 2p$ transition for a given donor species is characterized by a sharp line little shifted from its calculated position when inhomogeneous broadening is neglected. If, however, we attempt to calculate the actual $1s\rightarrow 2p$ line shapes using $n_I a_0^3 = 4\times 10^{-5}$ and the relative donor strengths and line centers as determined from magnetospectroscopic studies,[17] we find that the SIBT gives line shapes which are too broad near the peaks (so that only two of the three donor species in Fig. 6 are resolved in our calculated line shape) but much too narrow near the base.

The line which we have tentatively identified as $1s\rightarrow 3p$ has a certain qualitative similarity to Fig. 3, the observed peaks being symmetrical about the calculated unperturbed $1s\rightarrow 3p$ transition energy and the lower-energy peak having smaller peak amplitude than the higher-energy peak. One glaring quantitative discrepancy is that the peak-to-peak separation calculated is proportional to $n_I^{2/3}$ so that using the measured ionized impurity concentration of the sample in Fig. 3, the calculated separation of the $1s\rightarrow 3p$ peaks is 4.5 cm^{-1}; the measured separation is only ~ 1.2 cm^{-1} which, according to the SIBT, is characteristic of $n_I a_0^3 \cong 0.6\times 10^{-5}$. No central cell splittings are observed or expected in the $1s\rightarrow 3p$ transition because lines arising from each donor species are so broad that they completely overlap.

V. EFFECT OF MAGNETIC FIELD ON DONOR LIFETIMES

In this paper we have emphasized the limits of self-consistency of the SIBT approach to the linewidth problem. The inequalities (8) and (15), expressing these limits for the $n=2$ and $n=3$ states, respectively, are based on the requirement that the lifetimes of the excited states against field ionization in a uniform field be sufficiently long. We have concluded that the SIBT approach is not self-consistent for describing line shapes of absorption from the $1s$ to the $n=2$ levels at zero magnetic field in GaAs with n_I as low as 4×10^{13} cm^{-3}. Nevertheless, considerable success has been reported[1,2] in interpreting magneto-optical line shapes using GaAs samples with $4\times 10^{13} \lesssim n_I \lesssim 10^{14}$ cm^{-3}. We shall attempt here to sketch a semiquantitative explanation of how this can be so.

We show that the presence of a magnetic field, even if only of moderate strength, can reduce significantly the ionization probability of excited states of a hydrogenic atom in a uniform weak electric field.

Our approach is to employ the generalization, due to Oppenheimer,[18] of ordinary lowest-order time-dependent perturbation theory to the problem of tunneling. Oppenheimer shows that the probability of transition from an unperturbed bound state ψ_B to continuum free states ϕ_F of the same energy is given by

$$(2\pi/\hbar)|\langle\phi_F|H_2|\psi_B\rangle|^2\rho_F, \tag{26}$$

where H_2 is the perturbation responsible for the tunneling, ρ_F is the density of the states ψ_F with energy equal to the unperturbed bound state energy of ψ_B, and the ψ_F are eigenfunctions of a Hamiltonian obtained from the total Hamiltonian by evaluating it at points far away from the binding center. (Thus, in the case of a bound donor electron subject to the uniform electric field $\vec{F}/e$, the ψ_F are eigenfunctions of the Hamiltonian $p^2/2m^* - \vec{F}\cdot\vec{r}$.)

The special case of tunneling from the 1*s* state of a hydrogen atom in weak electric fields has been treated by a number of authors. The transition probability is given by Ref. 19 as

$$C(R/Fa_0)\exp(-\tfrac{4}{3}R/Fa_0), \tag{27}$$

where $F/|e|$ is the magnitude of the electric field and C is a numerical constant.

For small F the transition probability (27) is determined largely by the size of the exponential factor. We expect that this feature will persist in the more complicated problems to be considered here so that it will be sufficient to calculate the exponent of terms analogous to $\exp(-\frac{4}{3}R/Fa_0)$ above for making an educated guess at the critical-field strength appropriate to donors in combined magnetic and electric fields.

The general Hamiltonian describing a donor in the combined fields is

$$H = H_0 - e^2/\epsilon_0 r - \vec{F}\cdot\vec{r}, \tag{28}$$

where now

$$H_0 = p^2/2m^* + \tfrac{1}{2}\omega_c(xp_y - yp_x) + \tfrac{1}{8}m^*\omega_c^2(x^2+y^2), \tag{29}$$

with the cyclotron frequency $\omega_c = eB/m^*c$. We have used the symmetrical gauge in (29) and have assumed that the magnetic field $\vec{B}$ points in the z direction.

The bound states, ψ_B in (26), are eigenstates of $H_0 - e^2/\epsilon_0 r$. There is no known closed form representation for these states, but approximate expressions exist for a number of low-lying states including the experimentally prominent $2p_{-1}$ and $2p_0$ levels, of special interest to us. The direction of quantization defining these levels is now taken along the magnetic field since we are assuming henceforth

$$\hbar\omega_c \gg Fa_0. \tag{30}$$

We employ the following approximate wave functions (not normalized)

$$\begin{aligned}\psi_{2p_{-1}} &= (x - iy)\,e^{-\rho^2/8A^2}f(z),\\ \psi_{2p_0} &= z\,e^{-\rho^2/8A^2}f(z),\\ f(z) &= \exp[-K(z^2+\alpha^2)^{1/2}],\end{aligned} \tag{31}$$

where A, K, and α are optimized variationally for each magnetic field and level. These states are easy to work with; in addition, they give lower variational energies than the more familiar wave functions in which $f(z)$ is taken as e^{-z^2/b^2}. Nevertheless, the states (31) are inferior to, for example, trial functions of the type introduced in Ref. 20.

We shall consider separately two special conditions: (i) the electric field is perpendicular to the magnetic field ($\vec{F}\cdot\vec{B}=0$) and (ii) the fields are parallel ($\vec{F}\cdot\vec{B} = \pm FB$).

In case (i) the wave functions ϕ_F are eigenfunctions satisfying

$$(H_0 - Fy)\phi_F = E_F\phi_F, \tag{32}$$

where we have chosen, without sacrifice of generality, our y axis along the electric field direction. Exact solutions of (32) are well known for the case in which H_0 is written in the Landau gauge. We can employ these solutions in (32) if we multiply them by the factor $\exp(-im^*\omega_c xy/2\hbar)$. Eigenfunctions of (32) for the lowest Landau band have the form (not normalized)

$$\begin{aligned}\phi_F &= \exp(-im^*\omega_c xy/2\hbar)\exp[i(k_x x + k_z z)]\\ &\quad\times\exp[-(m^*\omega_c/2\hbar)(y - \hbar k_x/m^*\omega_c - F/m^*\omega_c^2)^2],\end{aligned} \tag{33}$$

with energy

$$\begin{aligned}E_F &= \tfrac{1}{2}\hbar\omega_c + \hbar^2k_z^2/2m^* - F(\hbar k_x/m^*\omega^2)\\ &\quad - F^2/2m^*\omega_c^2.\end{aligned} \tag{34}$$

An electron with wave function ϕ_F is localized in a slab of thickness $4r_c$ $[r_c \equiv (\hbar/2m\omega_c)^{1/2}]$ which is perpendicular to the electric field and centered at

$$\begin{aligned}y_0 &= \hbar k_x/m^*\omega_c + F/m^*\omega_c^2 \simeq \hbar k_x/m^*\omega_c\\ &= 2(k_x r_c)r_c.\end{aligned} \tag{35}$$

We have assumed $Fr_c/\hbar\omega_c \ll 1$. Neglecting terms proportional to k_z^2 and F^2 in (34) we find from conservation of energy that tunneling of a bound electron into the state ϕ_F can occur only if $E_B = F\,(\hbar k_x/m\omega_c) = 2Fr_c(k_x r_c)$ when E_B is the ionization energy of the bound electron in the magnetic field. Rewritten this condition becomes

$$k_x r_c = E_B / 2Fr_c \,. \tag{36}$$

As the electric field gets small, E_B/Fr_c becomes large; hence the overlap matrix element squared

$$|\langle \phi_F | (-Fy) | \psi_B \rangle|^2 \tag{37}$$

in (26) vanishes very rapidly. Using $\psi_{2p_{-1}}$ of (31) for the bound state function and ϕ_F given by (33) (but neglecting the term $F/m^* \omega_c^2$ in the exponent) we obtain for (37) in the limit $Fr_c/E_B \to 0$

$$|\langle \phi_F | (-Fy) | \psi_B \rangle|^2 \sim \kappa (E_B/Fr_c)^2 e^{-(E_B/Fr_c)^2/2} \,, \tag{38}$$

where κ is a constant independent of F.

The critical field is determined primarily by the exponential factor in (38), which is extremely sensitive to F for small F. For the $2p_{-1}$ state of GaAs shallow donors in a field near 65 kG, $E_B \simeq 0.9R$ and $r_c = (R/\hbar\omega_c)^{1/2} a_0 \simeq a_0/\sqrt{2}$. The factor $e^{-(E_B/Fr_c)^2/2}$ becomes approximately $e^{-(0.9R/Fa_0)^2}$. Although we cannot fix a critical field with any accuracy from the foregoing considerations, certainly $F_{\mathrm{crit}} a_0 > 0.1R$ and probably $F_{\mathrm{crit}} a_0 > 0.3R$. This is to be compared to Eq. (7) for the case of zero magnetic field. Clearly strong magnetic fields ($\hbar\omega_c \gtrsim R$) have a profound stabilizing effect on the $2p_{-1}$ donor levels against ionization in electric fields perpendicular to the magnetic field direction. Because of the increase in E_B and decrease of r_c with increasing magnetic field the transition probability is a monotonically decreasing function of magnetic field in the high-field region.

When the electric field is parallel to the magnetic field, the free eigenfunctions can be written, in the symmetrical gauge,

$$\begin{aligned} \phi_F &= (x - iy)\, e^{-(x^2+y^2)/8r_c^2} \Phi(-\xi) \,, \\ \xi &= (z/a_0 + \epsilon_z/Fa_0)(Fa_0/R)^{1/3} \,, \end{aligned} \tag{39}$$

where $\Phi(x)$ is the Airy function,[21] which has the important property

$$\lim_{x\to\infty} \Phi(x) = \frac{c}{2x^{1/4}}\, e^{-2x^{3/2}/3} \,. \tag{40}$$

The energy corresponding to ϕ_F is

$$E_F = \tfrac{1}{2}\hbar\omega_c + \epsilon_z \,,$$

where ϵ_z is a continuous eigenvalue associated with the motion of the electron along the electric (and magnetic) field direction. Conservation of energy in the tunneling requires

$$\epsilon_z = -E_B \,. \tag{41}$$

As $F \to 0$, therefore, $\xi \to -\infty$ and for z not too large we can replace Φ in (39) by its asymptotic form (40). The exponential factor in the F dependence of $|\langle \phi_F | (-Fz) | \psi_B \rangle|^2$ can be found by maximizing with respect to z the exponential function in the integrand of the z integral. The result is that the transition probability is proportional to

$$\exp\{-2Ka_0[E_B/R - \tfrac{1}{3}(Ka_0)^2]\,(R/Fa_0)\} \tag{42}$$

times factors which are sums of powers of F. It should be noted that the accuracy of the result (42) is subject to considerable uncertainty since the exponent which one obtains appears to be fairly sensitive to the form chosen for $f(z)$ in (31). We have evaluated (42) at various magnetic fields for both $2p_{-1}$ and $2p_0$ states. Thus, at 65 kG the exponent in (42) is $-1.1\, R/Fa_0$ and $-0.5\, R/Fa_0$ for the $2p_{-1}$ and $2p_0$ states, respectively. It would appear that these bound states are less stable for $\vec{F} \parallel \vec{B}$ than for $\vec{F} \perp \vec{B}$, as we would expect intuitively, but even for $\vec{F} \parallel \vec{B}$ they appear to be considerably more stable than the zero-field $n = 2$ levels.

With increasing magnetic field the $2p_{-1}$ level deepens more rapidly than the $2p_0$ and its ionization probability in an electric field of fixed strength likewise decreases more rapidly than that of the $2p_0$ level.

From the foregoing discussion we see how it is possible that the SIBT may be a good approximation for describing the high-field magneto-optical line shapes of a given sample while failing to describe the zero-field spectrum.

We do not wish to suggest that in fact the SIBT could be improved significantly by taking into account field ionization induced broadening of the donor lines in uniform electric fields. Such a model would itself suffer from the difficulty that electric fields from surrounding donor and acceptor ions are not uniform over the distance from the donor center to where the electron would emerge from the potential barrier, the barrier being calculated as if the electric field were uniform.

The exact nature of the electronic wave function produced when a relatively localized 1*s* electron donor is excited by photons with energy near $\frac{3}{4}R$ is not known. Presumably the breakdown of the SIBT is associated with delocalization of the excited electron—the electron being perhaps shared by one or more surrounding donor ions. We expect that magnetic field induced compression of the donor excited state wave functions would tend also to inhibit this kind of delocalization, which is driven by interdonor overlap of excited-state wave functions centered on neighboring donor ions.

---

*Work sponsored by the Department of the Air Force.

[1] D. M. Larsen, Phys. Rev. B 8, 535 (1973).

[2] D. M. Korn and D. M. Larsen, Solid State Commun. 13, 807 (1973).

[3] See for example, L. D. Landau and E. M. Lifshitz, *Quantum Mechanics Non-Relativistic Theory* (Perga-

mon, London, 1958).

[4] As can be checked from (3) and (4) the 1s level shift is negligible. We shall neglect throughout contributions of this level to the broadening.

[5] The constant β is given incorrectly in Ref. 1.

[6] D. F. Blossey, Phys. Rev. B 2, 3976 (1970).

[7] M. H. Rice and R. H. Good, J. Opt. Soc. Am. 52, 239 (1962).

[8] See Section IV of this paper, where the effect of strong magnetic fields on F_{crit} is discussed.

[9] L. V. Berman, Sh. M, Kogan, L. D. Saginov, V. I. Sidorov, and A. A. Telegin, Sov. Phys.-Semicond. 7, 1398 (1974) [Fiz. Tekh. Poluprovodn. 7, 2094 (1973)].

[10] The experimental line shapes presented in Ref. 9 do not show structure due to various residual donor species on the $1s \rightarrow 2p$ transition line. It seems possible that this structure was simply not resolved experimentally by the authors, since other workers using higher resolution and samples of presumably comparable purity have reported structure of the type shown in Fig. 6.

[11] Recall that the axis of quantization for the states of (5) is the electric field direction and that this direction varies from neutral donor to neutral donor. Thus, on average, the $2p_0$ level contributes the same oscillator strength as the $2p_{+1}$ and $2p_{-1}$ levels, assuming that we can neglect the level shifts compared to $\frac{3}{4}R$.

[12] This result is immediately obvious by inspection of the unperturbed hydrogenic wave function in parabolic coordinates (see Ref. 3)

$$\psi_{n,0,(n-1)/2,(n-1)/2}$$
$$= \text{const} \times f_{(n-1)/2}(r-z)\, f_{(n-1)/2}(r+z).$$

For the $|m| = 1$ states with n even we have

$$\psi_{n,\pm 1,n/2-1,n/2-1}$$
$$= \text{const} \times (x \pm iy) f_{(n/2)-1,\pm 1}(r-z)\, f_{(n/2)-1,\pm 1}(r+z)$$

which obviously has odd parity.

[13] The opposite effect is found in the distribution of $\partial \mathcal{E}_z / \partial z$; the correlated distribution tends slightly to have larger values of $\partial \mathcal{E}_z / \partial z$ than the uncorrelated.

[14] All comparisons between correlated and uncorrelated distributions are made here using identical arrangements of charged ions around the neutral donors for both distributions.

[15] These data are from D. M. Korn and G. E. Stillman (private communication).

[16] H. R. Fetterman, D. M. Larsen, G. E. Stillman, and P. E. Tannenwald, Phys. Rev. Lett. 26, 975 (1971).

[17] G. E. Stillman, D. M. Larsen, C. M. Wolfe, and R. C. Brandt, Solid State Commun. 9, 2245 (1971).

[18] J. R. Oppenheimer, Phys. Rev. 13, 66 (1928).

[19] See Ref. 3, p. 258.

[20] D. M. Larsen, J. Phys. Chem. Solids 29, 271 (1968).

[21] See, for example, Ref. 3, pp. 70–72 and pp. 491–492.