PHYSICAL REVIEW B **67**, 165204 (2003)

Concentration broadening of absorption lines from shallow donors in multivalley bulk semiconductors

David M. Larsen
University of Massachusetts Lowell, Lowell, Massachusetts 01854

(Received 9 December 2002; published 17 April 2003)

Concentration broadening of donor absorption lines is studied by numerical simulation at donor densities so low that overlap of the wave functions of electrons bound to different donors is completely negligible. At such densities broadening of donor absorption lines due to overlap is replaced by broadening due to resonant van der Waals interaction between donors, an effect which produces linewidths proportional to the first power of the donor concentration. It is argued that in three dimensions, but not in two, the van der Waals interaction completely delocalizes the excitation induced by the absorption of a photon by the donor system initially in its ground state. Detailed line-shape calculations are made for P donors in Si. For that donor species the concentration broadened $1s \rightarrow 2p_{\pm}$ transition line is predicted to be 32% broader than the zero-density (lifetime-broadened) line at a P concentration of 1×10^{16} donors/cm^3 whereas the $1s \rightarrow 2p_0$ transition at the same P density is only 8% broader. Comparison is made with available data.

DOI: 10.1103/PhysRevB.67.165204 PACS number(s): 71.55.Cn, 78.30.Am

I. INTRODUCTION

Low-temperature experiments on high-purity uncompensated *n*-type bulk samples of the multivalley semiconductors Si and Ge reveal numerous narrow absorption lines. Absorptions to the lower-lying excited states in Si are reported[1] to have, typically, full widths at half maximum of 0.02–0.03 meV at donor concentrations near 10^{14} donors/cm^3; the broadening of the narrowest lines is attributed to the spontaneous emission of acoustic phonons from the excited state with the electron falling either to the ground state or a lower-lying excited state. Such a process would give rise to a Lorentzian line with full width at half maximum (FWHM) equal to 2Γ where Γ is the decay constant of the excited state reached in the optical transition. An increase of 0.004 meV in linewidth of the $1s \rightarrow 2p_0$ transition at densities of 2 or 4 $\times 10^{15}$ donors/cm^3 is reported in Si:P (Si doped with phosphorus donors), but the measurements do not definitively establish the amount of concentration-induced broadening since error bars quoted for each linewidth determination are ± 0.002 meV.

Magneto-optical measurements in Ge give FWHM values for the $1s \rightarrow 2p_-$ transitions as small as 0.008 meV for the stress-insensitive D(H,O) donor complex and 0.027 meV for substitutional P donors[2] at concentrations of 10^{11} donors/cm^3. The D(H,O) lines are observed to be Lorentzian, and their width is attributed to lifetime broadening as described above.

Although as far as the author is aware, systematic high-resolution measurements of linewidth vs concentration are not available at low donor concentrations (say, $\leqslant 10^{16}$ donors/cm^3 in Si) it is evident that with increasing concentration the lines broaden and eventually develop structure in their low-energy tails, likely associated with overlap of electrons from nearest-neighbor donor pairs.[3] However, the experimental situation is not completely clear even in the relatively well-studied case of Si:P. There appears, for example, to be a major discrepancy in the linewidths reported in Refs. 1 and 3, the latter plotting lines much wider than reported in the former at a comparable donor concentration ($\approx 4 \times 10^{15}$ donors/cm^3).

In this paper the broadening of dipole-allowed donor transitions induced by Coulomb interactions between neutral donors is studied in dilute systems, where the donor centers are widely separated. To isolate the leading term in the concentration broadening of a system of donors in random positions the Coulomb interaction between them is expanded in powers of the ratio of the ‘‘radius’’ of the donor wave function to the separation of the donor centers. Only the lowest-order nonvanishing contribution to the shift in transition energy is kept. Its contribution to the broadening is then calculated for dipole transitions originating from the ground state of the donor system. In the case of Si and Ge the most prominent of the observed transitions are $1s \rightarrow np_0$ or $1s \rightarrow np_{\pm}$. Detailed calculations are carried out for the case of Si:P for the $1s \rightarrow 2p_0$ and $1s \rightarrow 2p_{\pm}$ transitions.

There are two calculations previously reported that are similar in spirit to the one to be presented, although both are concerned with the van der Waals interaction in donors in GaAs, which has a single conduction-band minimum. The first deals with the relatively simple case of donors in a magnetic field, where broadening of the $1s \rightarrow 2p_-$ transition is studied in bulk samples.[4] The second considers effects on the impurity cyclotron resonance line due to van der Waals interactions between barrier impurities in a two-dimensional quantum well model.[5] Features of the present calculations include consideration of interactions between electrons in different anisotropic valleys, which is not relevant for semiconductors with a single conduction-band minimum, and taking into account the effect of central cell corrections, which have been neglected for the very shallow donors found in GaAs and related compound semiconductors.

Briefly, the results obtained indicate that, in the absence of other broadening mechanisms, the low-density concentration dependence of the broadening of the donor species of interest is proportional to the density of that donor species, independent of the density of any other donor species that might also occur in the same sample (assuming that the central cell corrections of the two species are not equal or nearly equal to each other). Unlike broadening associated with overlap of electrons on different donors, the concentration broadening predicted here, being proportional to the squared transition dipole matrix element from the ground state, tends to be weaker for transitions to more highly excited states than to lower-lying excited states of the same symmetry. The predicted FWHM due to concentration broadening alone is donor-species dependent, increasing with decreasing central cell correction, but, for low concentrations, is much smaller than the observed linewidths. It is assumed that another process, which is concentration independent (presumably lifetime broadening), is responsible for the bulk of the observed broadening at low densities. The effect of concentration broadening is found by convolving the predicted concentration-broadened spectrum with a Lorentzian line representing the lineshape at zero donor density. Although the predictions are not inconsistent with the experimental results of Ref. 1, there is not at present sufficiently detailed experimental information to definitively test the present theory.

II. THEORY

The Coulomb interaction between donors i and j with centers separated by a displacement $\mathbf{R}_{i,j}$ is given by the expression

$$\frac{e^2}{\epsilon_0}\left(\frac{1}{|\mathbf{R}_{i,j}+\mathbf{r}_i-\mathbf{r}_j|}-\frac{1}{|\mathbf{R}_{i,j}-\mathbf{r}_j|}-\frac{1}{|\mathbf{R}_{i,j}+\mathbf{r}_j|}+\frac{1}{R_{i,j}}\right). \qquad (1)$$

where $\mathbf{r}_i$ is the displacement of the ith electron from the center of the ith donor; the magnitude of this displacement is understood to be of the order of the "donor radius," r_{donor}. The first nonvanishing term in the expansion of Eq. (1) in inverse powers of $R_{i,j}$ is the van der Waals term, given by

$$H_{VW}(i,j)=\frac{e^2}{\epsilon_0 R_{i,j}^3}\left[r_i\cdot r_j-\frac{3(R_{i,j}\cdot r_i)(R_{i,j}\cdot r_j)}{R_{i,j}^2}\right]. \qquad (2)$$

This interaction couples a two-donor state in which donor i is in a p state with donor j in its ground state, to a second state in which donor i is in its ground state and donor j is in an equivalent p state. (The p states of a donor have a nonvanishing dipole matrix element to the ground state.) These coupled states are degenerate for isolated donors; their common energy is equal to the sum of the ground-state energy and the p-state energy for an isolated donor. H_{VW} splits the degeneracy, leading to an energy shift of order $(e^2/\epsilon_0 R_{i,j})(r_{\mathrm{donor}}^2/R_{i,j}^2)$. Thus, the leading term in the shift of the excitation energy due to the Coulomb interaction between two neutral donors at large separations (low density) is provided by H_{VW}. This paper studies the effect of H_{VW} on the spectral line shape of dilute donors.

To understand the effect of H_{VW} on the spectrum of weakly excited donors in Si or Ge it is useful to review briefly certain pertinent facts about the nature of the ground state and p states of isolated donors in these materials.[6,7] Effective-mass theory is very accurate for describing the p states but is not generally sufficient for the ground state, since it predicts, contrary to experiment, that the ground state of isolated donors is degenerate, each degenerate state being characterized by an s-like envelope function associated with a different conduction-band minimum. In the case of substitutional donors this degeneracy is broken by valley-orbit interaction which splits off the true, nondegenerate, completely symmetric ground-state function, denoted as the $1s(A1)$ state. The energy separation of this $1s(A1)$ state from any other donor state is much larger than the energy shifts induced by H_{VW}. Valley-orbit interaction is negligible for the p states. If the effective mass of electrons in the valleys were isotropic the p states associated with each valley would be triply degenerate (as in the elementary picture of the hydrogen atom). However, in both Si and Ge each valley has an anisotropic effective mass which partially breaks the threefold p-state degeneracy producing a degenerate pair, np_+ and np_-, and a deeper split-off singlet state, np_0, associated with that valley. This p-state splitting also turns out to be much larger than energy shifts induced by H_{VW}.

For each value of n there are six degenerate np_0 states in Si [corresponding to two conduction-band minima along each of the directions (1,0,0), (0,1,0), and (0,0,1) in $\mathbf{k}$ space] and four for Ge [corresponding to one conduction-band minimum at the zone boundary along each of the directions (1,1,1), (−1,1,1), (1,−1,1), and (−1,−1,1)]; each of these p states is associated with a single valley and has a nonzero dipole matrix element to the ground state. Likewise there are twelve degenerate $np_\pm$ states for Si and eight for Ge. To describe the interaction of two donors due to H_{VW} in Eq. (2) when one donor is in an excited np_0 state and the other is in the $1s(A1)$ state would appear to require diagonalizing H_{VW} in a set of twelve basis states for Si (to realize all the possibilities of one donor in the ground state and the other in one of the six possible np_0 states) and eight for Ge. Likewise 24 basis states for Si and sixteen for Ge would seem to be required for the analogous problem involving the $np_\pm$ states. (Actually, for Si it can be shown that only three of the six valleys need be included, one for each of the directions associated with the conduction-band minima. Thus for Si only six basis states for np_0 and twelve for $np_\pm$ are required.)

Finding the wave functions and energy spectrum of the coupled two-donor system is an exercise in degenerate perturbation theory. It is convenient to employ basis states of the form

$$|np,l\rangle_j\times|1s(A1)\rangle_i,\quad |np,l\rangle_i\times|1s(A1)\rangle_j, \qquad (3)$$

where i and j are donor subscripts, np refers either to an np_0 state (if transitions $1s\rightarrow np_0$ are of interest) or to either an np_- or np_+ state (if transitions $1s\rightarrow np_\pm$ are required), and the index l labels the valley with which the p state is associated (more exactly, l labels the valley Bloch function multiplying the np envelope function). The Hamiltonian matrix constructed from H_{VW} and these basis functions is then diagonalized.

Matrix elements of H_{VW} in the basis states of Eq. (3) for Si donors for transitions from the ground state to $2p_0$ have the form

$$\frac{e^2}{\epsilon_0}\frac{|\langle 1s|z|np_z\rangle|^2}{3}F(\mathbf{R}_{ij};\alpha,l;\beta,l')/R_{ij}^3, \tag{4a}$$

where $|1s\rangle$ and $|np_z\rangle$ are, respectively, the envelope functions for the $1s$ and np_0 states in the (0,0,1) valley (where the z direction is the heavy-mass direction); the indices l and l' label the valleys occupied by the excited-state electron belonging to donors i and j. Here l or $l'=1-3$ refer to valleys along the x, y, and z directions, respectively [or equivalently the (1,0,0), (0,1,0), and (0,0,1) crystallographic directions, respectively]. When l and l' are equal, the excited electrons of the coupled donors are in the same valley, otherwise they are not. The indices α or β identify which *np* state is excited; these indices assume possible values 1, 2, or 3 corresponding, respectively, to np_x, np_y, or np_z excited states. In Eq. (4a),

$$\alpha=l, \quad \beta=l'.$$

Likewise for transitions to $np_\pm$ the matrix elements are

$$\frac{e^2}{\epsilon_0}\frac{|\langle 1s|x|np_x\rangle|^2}{3}F(\mathbf{R}_{ij};\alpha,l;\beta,l')/R_{ij}^3. \tag{4b}$$

In Eq. (4b) there are two values of α for each value of l and similarly two values of β for each l'. This follows from the requirement that α and β run over all of their possible values subject to the inequalities

$$\alpha\neq l, \quad \beta\neq l'.$$

All envelope functions in the matrix elements of Eqs. (4a) and (4b) are those for states in the (0,0,1) valley (although the formulas apply to all valleys). Since no magnetic field is present we have replaced in Eq. (4b) the *np*-state basis set np_+ and np_- by the more convenient set np_x and np_y, where x and y lie along (1,0,0) and (0,1,0), respectively. [Note that in the (0,0,1) valley $\langle 1s|x|np_x\rangle=\langle 1s|y|np_y\rangle$]. The factor of $\frac{1}{3}$ in Eqs. (4a)–(4b) arises from the uniform weighting of the $1s$ envelope functions in each of the three valleys in the $1s(A1)$ split-off ground state. Formulas for the F functions are given in Appendix A; it will suffice here to note that these functions depend only on the angles of $\mathbf{R}_{ij}$. The matrix elements appearing in Eqs. (4a)–(4b), which involve envelope functions, are discussed in Appendix B. They are sensitive to the central cell correction of the donor species of interest, since the $1s$ envelope function must be modified from the form predicted by effective-mass theory to account for the extra central cell binding. Such a correction to the effective-mass $1s$ wave function for P donors in Si reduces significantly the matrix elements of Eqs. (4a)–(4b).

The generalization from two donors to N donors is straightforward. For N donors the problem is to find the absorption line shape for a single photon incident upon a sample of volume V containing a dilute system of N donors, all of which are initially in the ground state. The donor density n_d is defined by

$$n_d=N/V.$$

The excited-state basis functions analogous to those of Eq. (3) are

$$\phi_i(np,l)=|np,l\rangle_i\prod_{j\neq i}^{N}|1s(A1)\rangle_j, \tag{5}$$

where n is fixed and $|np,l\rangle_i$ ranges over all donors ($1\leq i\leq N$) and all possible degenerate *np* states; l labels the valley occupied by the electron in the *np* state. In Si there are $3N$ such basis functions for transitions to an np_0 state and $6N$ for $np_\pm$ transitions. If separations between donor centers are measured in units of $n_d^{-1/3}$, as is the convention henceforth in this paper, then by virtue of the R^{-3} dependence of the matrix elements indicated in Eqs. (4a) and (4b), all matrix elements between these basis functions for a given transition share a common factor,

$$v_0=\frac{e^2}{\epsilon_0}n_d|\langle 1s|z|np_z\rangle|^2/3 \tag{6a}$$

for np_0 transitions and

$$v_\pm=\frac{e^2}{\epsilon_0}n_d\langle 1s|x|np_x\rangle|^2/3 \tag{6b}$$

for $np_\pm$ final states. These quantities, v_0 and $v_\pm$, serve, therefore, as scale factors for their respective energy spectra. The spectral shapes inferred from diagonalizing H_{VW} in the basis functions of Eq. (5) are universal for donors in Si which have ground states of symmetry $1s(A1)$, being independent of the density of donors and the quantum number *n*. On the other hand the line breadth is linear in n_d (and depends on *n* through the matrix elements).

Spectra are constructed from the wave functions and energies calculated in a way already described in Ref. 5. Donor samples are modeled by filling a sphere with N donors scattered at random throughout the spherical volume. The radius of the sphere R_S is set so that $n_d=1$ [$R_S=(3N/4\pi)^{1/3}$]. The matrix of H_{VW} is set up and diagonalized, with both energies and wave functions recorded for each sample. Each energy eigenvalue is weighted in proportion to the square of its associated dipole transition matrix element, $|e\langle\psi|(\Sigma_{i=1}^N x_i)|1s(A1)\rangle|^2$, where $|\psi\rangle$ is the eigenfunction associated with the eigenvalue considered [here, linearly polarized light along (1, 0, 0) is assumed, but the direction of polarization is immaterial]. Using these weights histograms of the energy are plotted for a sufficient number of different random samples to produce a smooth curve. It was noted that as the sample size (N) increased the predicted spectral shape became broader, caused almost entirely by a decrease in relative spectral strength near the unperturbed transition energy (a similar effect was noted in Ref. 4). The maximum values of N employed in the present work were 250 and 500, for $1s\rightarrow np_\pm$ and $1s\rightarrow np_0$ transitions, respectively. Convergence studies at different N values suggest that spectral linewidths using these maximum values of N attain values within, perhaps, a few percent of those which would have been computed from an arbitrarily large sample. However, it is difficult to be sure about this.

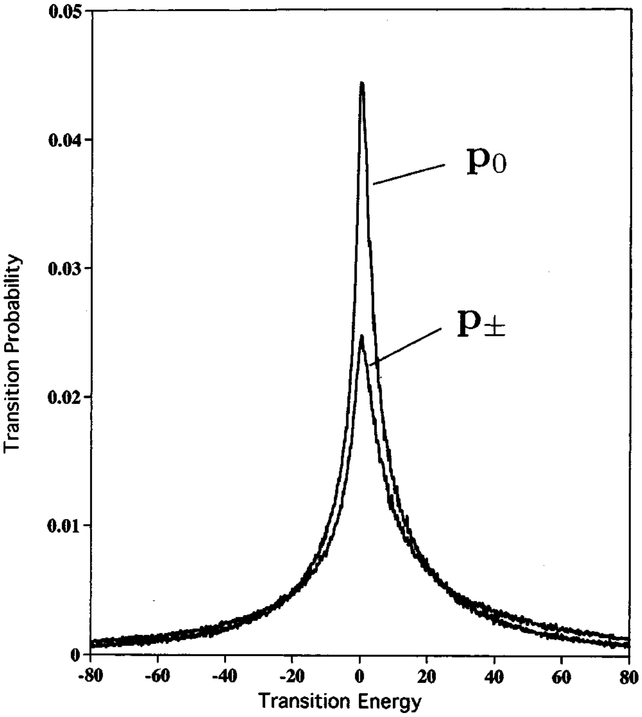

FIG. 1. Predicted normalized line shapes for pure van der Waals broadening in Si of the $1s(A1)\rightarrow np_0$ absorption (curve labeled p_0) and the $1s(A1)\rightarrow np_\pm$ (curve labeled $p_\pm$). Infinite lifetime is assumed for the excited state. The zero of energy for each curve is at the isolated donor transition energy. The appropriate energy scale for any particular transition is found by multiplying the energy scale shown by $v_0/2$ or $v_\pm/2$, respectively. Approximately 1600 and 3000 different random donor configurations with N equal to 500 and 250, respectively, were employed in calculating the curves shown. These curves are interpolated from histograms produced by the numerical simulation with energy box sizes equal to 0.2.

To obtain the transition energy one need merely subtract the unperturbed ground-state energy from the calculated energies of the one-photon excited states. The unperturbed ground-state energy is used because concentration broadening of the ground state is of higher order in n_d than that of the excited state and so can be neglected at low donor densities. If one performs this subtraction in each diagonal element of the matrix, those elements all become equal to the unperturbed transition energy of the donor, and the eigenvalues of the matrix directly give the possible transition energies. (Note that if two donor species are present with sufficiently different central cell corrections then their transition energies will likewise be very different. As a result, donors of one species can couple only very weakly to those of the other and, to a good approximation, transitions associated with each donor species will be broadened as if the other species were not present.)

Spectra based on the foregoing theory are shown in Fig. 1 for both $1s\rightarrow np_0$ and $1s\rightarrow np_\pm$ transitions. Zero energy on the graph corresponds to the unperturbed donor transition energy for both of these transitions. The energy scale recorded is for $v_0=v_\pm=2$, whereas the calculated values for the scale factors v_0 and $v_\pm$ as discussed in Appendix B are only 5.1×10^{-5} and 13×10^{-5} meV, respectively, for transitions to $2p$ states in Si with $n_d=4\times10^{15}$ donors/cm^3. Based on these calculated values the predicted full widths at half maximum for both $1s\rightarrow 2p_\pm$ and $1s\rightarrow 2p_0$ transitions in Si:P are much smaller than those reported in Ref. 1. Moreover, the experimental widths show a much weaker than linear dependence of the widths with n_d. It is clear, as has been recognized in Refs. 1 and 2, that in the high-purity donor samples of those references there is at least one other source of broadening that dominates the concentration broadening. Both references suggest that one such broadening mechanism likely to be of importance is the decay of donor excited states via spontaneous emission of acoustic phonons. Such decay processes result in Lorentzian lines with values of FWHM of 2Γ, which are much larger than the FWHM inferred from the scale factors and line-shape curves for pure concentration broadening at values of n_d less than or near 4×10^{15} donors/cm^2 in Si.

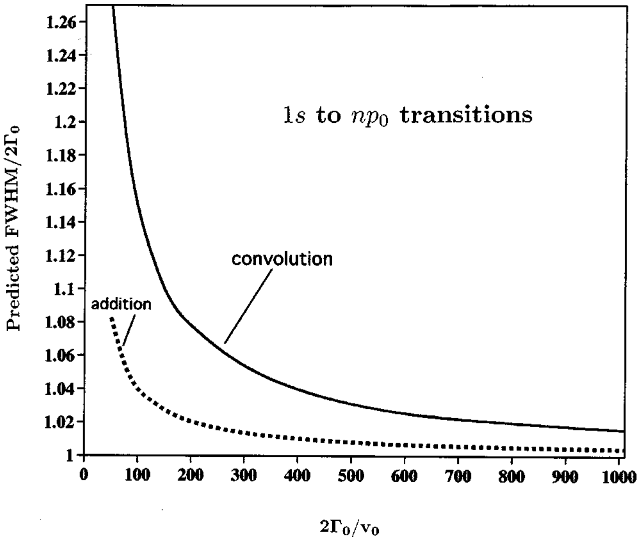

FIG. 2. The FWHM of the predicted concentration-broadened line in units of the FWHM of the donor line at vanishing donor density $(2\Gamma_0)$ vs $2\Gamma_0/v_0$ for $1s\rightarrow np_0$ donor transitions in Si:P (solid line). The quantity v_0 is a measure of the strength of the van der Waals interaction pertinent to transitions to the np_0 states and is defined in Eq. (B2a). The dashed line shows the result obtained by simply adding the FWHM values for each of the unconvolved curves.

To study the effect of concentration broadening on the observed lines in Si:P it is necessary to include both concentration and lifetime broadening simultaneously. This can be done by convolving line shapes of Fig. 1 with Lorentzian lines of appropriate width. (Of course, convolution is allowed only if the two broadening mechanisms are independent.[9]) Figures 2 and 3 summarize the results of the convolution calculations for the linewidths. These graphs predict the fractional increase of the zero-concentration FWHM for a given ratio $2\Gamma_0/v_0$ or $2\Gamma_\pm/v_\pm$, where Γ_0 and $\Gamma_\pm$ are half widths of the $1s\rightarrow np_0$ and $1s\rightarrow np_\pm$ transitions, respectively, of isolated donors. These plots convey the important result that the FWHM of the convolved line is always significantly greater than the sum of the FWHM values of each of the unconvolved lines. It should be noted that widths

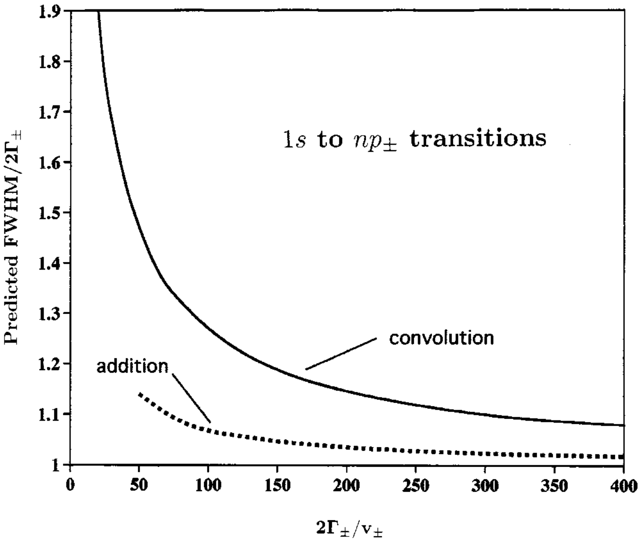

FIG. 3. The FWHM of the predicted concentration-broadened line in units of the FWHM of the donor line at vanishing donor density ($2\Gamma_{\pm}$) vs $2\Gamma_{\pm}/v_{\pm}$ for $1s \rightarrow np_{\pm}$ donor transitions in Si:P (solid line). The quantity $v_{\pm}$ is a measure of the strength of the van der Waals interaction pertinent to transitions to the $np_{\pm}$ states and is defined in Eq. (B2b). The dashed line shows the result obtained by simply adding the FWHM values for each of the unconvolved curves.

of the convolved lines are considerably less sensitive to the value of N chosen in their calculation than are the lines of Fig. 1.

To apply the predictions of Figs. 2 and 3 to the results of Ref. 1 one can see that, for the data at lowest densities quoted ($\approx 10^{14}$ donors/cm^2), the expected concentration broadening is negligible for the $1s \rightarrow 2p_0$ transition and small for $1s \rightarrow 2p_{\pm}$; to a good approximation one can set the observed FWHM at lowest density (1 or 2×10^{14} donors/cm^3) to 2Γ. The present theory predicts a $\approx$4% increase in linewidth for the $1s \rightarrow 2p_0$ transition at 4×10^{15} donors/cm^3 compared to pure lifetime broadening. Although the data[1] seems to show a bigger effect than this, the error bars are sufficiently large that a $\approx$4% effect could not be excluded.

It would appear that the $1s \rightarrow 2p_0$ absorption is not the ideal transition for study of concentration broadening in high-purity n-Si. A much larger increase is predicted (14%) for the $1s \rightarrow 2p_{\pm}$ transition at the same donor density (4×10^{15} donors/cm^2) but, unfortunately, to our best knowledge, published data to test this prediction is not available in Ref. 1 or elsewhere at the time of this writing.

III. LOCALIZATION

An interesting question is whether the excitation of donors produced by the absorption of a single photon is localized or extended. A "localized" eigenstate in this paper means an eigenstate for which it is possible to enclose essentially all excited donors in a sphere of sufficiently large but finite radius. [For example, one might require that for any positive nonzero number ϵ, however small, it is always possible to find a sphere sufficiently large that the sum of the squared amplitudes of the basis functions of Eq. (5) that correspond to donors lying outside the sphere is less than ϵ in the eigenvector of interest.]

One way to approach this question in a simulation is to assume that the exciting light falls only upon a single donor (rather than the whole sample) and investigate the probability of finding donors excited at various distances from that single donor. The light is to be taken to have uniform intensity over a spectral range broad enough to encompass essentially the whole absorption line. A simulation of this type has been performed in which the single donor being excited by incident photons, having been assigned the index 1, is placed in the center of a spherical sample constructed as described earlier. The eigenvectors of H_{VW} are calculated and the probability of finding the ith donor excited, $P(i)$, where $i > 1$, is calculated according to the formula

$$P(i) = \sum_{j=1}^{N} |c_1^{(j)}|^2 |c_i^{(j)}|^2,$$

where $c_i^{(j)}$ is the amplitude for excitation of the ith donor in the jth eigenfunction. In this simulation the probability of exciting the jth eigenfunction itself is $|c_1^{(j)}|^2$. The distance of the ith donor from the center of the sphere is then entered into the histogram with the weight $P(i)$ assigned to it.

To keep the computations manageable the one-valley model of Ref. 4 was employed, where, in the notation of Appendix A,

$$H_{VW} = (1 - 3Z^2/R^2)/R^3.$$

Results for the probability per unit length averaged over many random donor distributions are plotted in Fig. 4 for sample sizes $N = 100$ and 1000. Of particular interest is the steadily rising probability as one approaches the sample boundary, evident for both sample sizes. One can hardly avoid interpreting this behavior as evidence of extended states. The sharp peak at small distances corresponds primarily to excitation of a donor pair consisting of the central donor and its close-lying nearest neighbor. From the discussion to follow it is expected that as $N \rightarrow \infty$ this peak will narrow and disappear as even excited states associated with those rare pairs which are very closely spaced (and have energies far out in the tail of the lines) delocalize in sufficiently large samples.

Sharply contrasting results are presented in Fig. 5 for the van der Waals interaction in two dimensions. The two-dimensional (2D) van der Waals Hamiltonian employed is that of Ref. 5,

$$H_{VW}^{(2D)} = -1/R_{i,j}^3,$$

where $R_{i,j}$ is the distance in the x-y plane between donors i and j. The diagonal elements are all zero. Only small differences can be found between the radial dependence of excitation for the small and large samples (at distances for which they can be compared). For both sample sizes the probability of finding excited donors farther away from the illuminated donor than, for example, the average nearest-neighbor

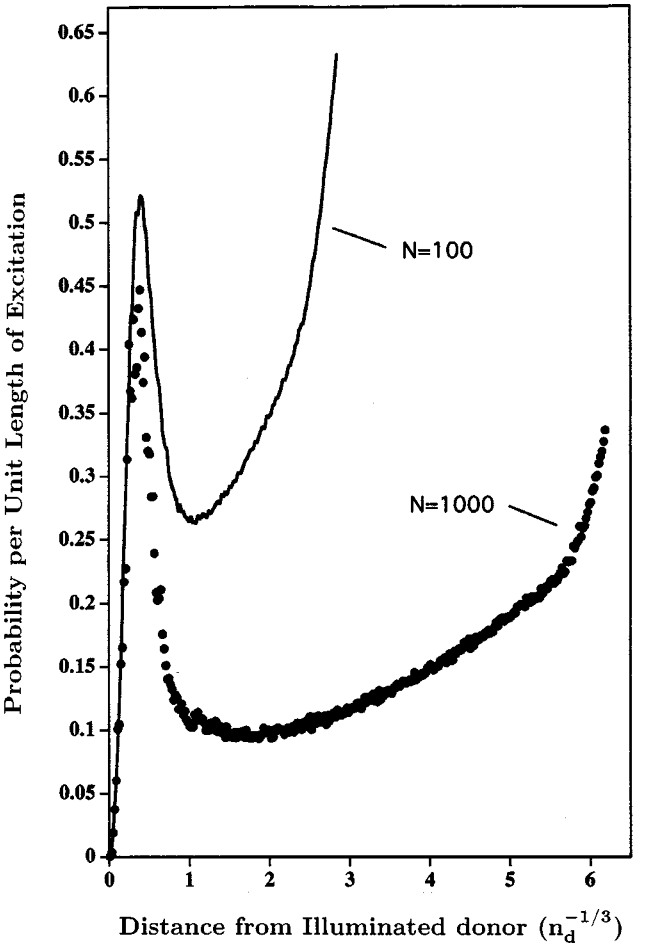

FIG. 4. Probability per unit length, in three dimensions, of finding an excited donor vs distance (units of $n_d^{-1/3}$) from the single illuminated donor at the center of a spherical sample. The curves terminate at the boundary of the spheres enclosing the donors. The interpolated curve is for $N=100$, calculated with 205 000 samples; the dots represent results for $N=1000$ with 7700 samples. The histogram bin size is 0.02 in both cases, and the curves are normalized to the unit area.

distance (0.5 on the distance axis of Fig. 5) tends to decrease with distance. (The rise near the sample edge for $N=100$ samples appears to be an artifact of small sample size, since no comparable effect is found for the $N=1000$ samples.) Behaviors of this sort suggest that the van der Waals excitations are localized in two dimensions, as concluded in Ref. 5.

To understand these results in a simple way it is useful to review how quantum states that are close in energy mix when coupled by a perturbation. If ξ_1 and ξ_2 are normalized eigenstates of some unperturbed Hamiltonian which have a common energy E, and are coupled by the perturbation H', which has zero diagonal elements in those eigenstates, then the resulting eigenstates are completely mixed combinations of both, namely, $(\xi_1+\xi_2)/\sqrt{2}$ and $(\xi_1-\xi_2)/\sqrt{2}$ with energies $E+M$ and $E-M$, respectively, where $M=\langle\xi_1|H'|\xi_2\rangle$. Should the unperturbed energies of ξ_1 and ξ_2 be not exactly equal to each other but differ by an amount ΔE, then if $|\Delta E|$ is less than or of the order of $|M|$ substantial mixing still occurs, the mixing becoming weaker as the ratio $|M/\Delta E|$ gets smaller.

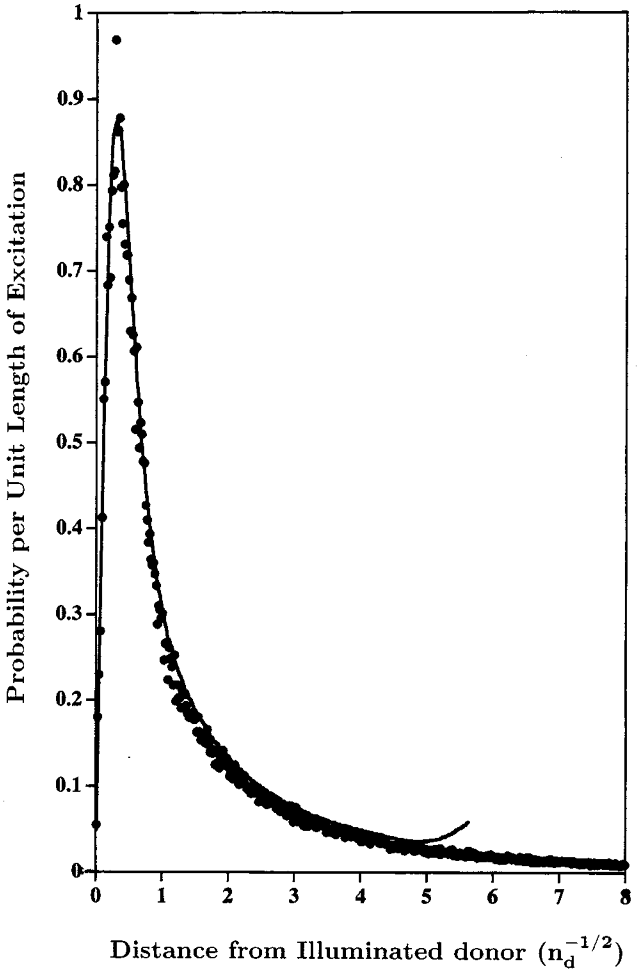

FIG. 5. Probability per unit length, in two dimensions, of finding an excited donor vs distance (units of $n_d^{-1/2}$) from the single illuminated donor at the center of a circular sample. The curve for $N=100$ terminates at the boundary of the circle enclosing the donors. The interpolated curve is for $N=100$, calculated with 1.2×10^6 samples; the dots represent results for $N=1000$ with 10 400 samples. The histogram bin size is 0.02 in both cases, and the curves are normalized to the unit area.

The eigenfunctions of an infinite system of donors, with finite uniform density, which has absorbed one photon from its ground state can be written as a linear combination of the basis states given by Eq. (5). For example, in Si the normalized eigenvectors of the $2p_0$ donor excited states have the form

$$\sum_{i=1}^{N}\sum_{l=1}^{3} c_{i,l}(2p_0)\phi_i(2p_0,l),$$

where $c_{i,l}(2p_0)$ is the probability amplitude for finding the ith donor excited to the $2p_0$ state in valley l. Consider such an eigenvector corresponding to an arbitrary eigenvalue E. Let it be assumed, contrary to the evidence already presented, that to an excellent approximation only a finite number of donors (a ‘‘donor cluster’’) are excited in this eigenvector, irrespective of the value of E. (Notice that the excitation is, by that assumption, localized in space, since a finite number of donors can occupy only a finite volume of space.) For every value of E, then,

$$\sum_{\text{subset}} \sum_{l=1}^{3} |c_{i,l}|^2 = 1,$$

where the sum is over the finite subset comprised of the excited donors. The eigenvector associated with E is also an eigenvector of an ‘‘unperturbed’’ van der Waals Hamiltonian, which includes couplings only among the members of the subset.

Let it also be assumed that the distribution of energies of the clusters is continuous. Then, given a cluster of energy E, one can search for other clusters with energy close to E, say, with energy between E and $E+\Delta E$, located at a distance R from the first cluster, where R is much greater than any linear dimension of any cluster. Such distant clusters will be coupled to the given cluster by matrix elements of H_{VW}, which the elements act as the perturbing Hamiltonian and are all of order R^{-3}. The number of such clusters between R and $R+\Delta R$ is proportional to

$$4\pi R^2 \Delta R \Delta E$$

in three dimensions and to

$$2\pi R \Delta R \Delta E$$

in two dimensions. These clusters will mix significantly with the given cluster if ΔE is smaller than or of the order of the matrix element of H_{VW} coupling the clusters. Thus ΔE can be as large as order R^{-3} and still allow significant coupling between the clusters. The number of such clusters in three dimensions is then proportional to $4\pi R^{-1}\Delta R$, which diverges logarithmically upon integration to infinity, whereas the number in two dimensions is only proportional to $2\pi R^{-2}\Delta R$, which gives a finite result upon such integration. In three dimensions, then, there are an infinite number of clusters strongly coupled to the original cluster; these cannot be enclosed in a finite volume so it is clear that the excitation must spread throughout the infinite system, contrary to the initial assumption. In two dimensions, however, there are only a finite number of clusters that couple strongly to a given cluster. Whether excitations can percolate through the system under such circumstances is not obvious from the argument above, which gives only a sufficient condition for the appearance of extended states. The computer experiments reported here and in Ref. 5 suggest that they cannot.

IV. CONCLUSION

This paper has shown how the interaction of electrons on two identical but widely separated donors causes transfer of excitation from one donor to the other. Such transfers are associated with a broadening of donor absorption lines which is linear in the donor density and, in the low-density limit, predominates over mechanisms of concentration broadening connected to overlap of donor wave functions. Detailed calculations have been presented for P donors in Si, where the predicted broadening at low densities is small compared to measured widths. It has been assumed that the zero-density broadening is Lorentzian and independent of the positions of the donors (as would be the case for lifetime broadening) so that the concentration effect can be found by convolution. Other possible mechanisms that might contribute to the broadening of donor lines at very low donor densities, such as random strains due to electrically inactive impurities, dislocation lines,[1,2] or statistical fluctuations of mean isotopic composition at different donor neighborhoods have not been considered. However, these broadenings would likely be only weakly, if at all, correlated with the positions, relative to each other, of the donors that produce the observed spectra. Thus the convolution method of this paper should be applicable, a least as a first approximation, but the actual line shape of the donor absorption at donor densities where the van der Waals interaction is negligible should be used instead of the Lorentzian shape applied here. Small concentration-induced increases in linewidth are found in the simulation reported here for the $1s \rightarrow 2p_0$ transition, which, given the error bars on the present data,[1] is not inconsistent with that data. A significantly stronger concentration-dependent broadening is predicted for the $1s \rightarrow 2p_\pm$ transition. That prediction awaits experimental test.

Computer experiments supported by heuristic arguments indicate that the eigenstates of excited donors are extended in three dimensions, but localized in two.

APPENDIX A

This appendix lists the functions F in Si required for Eqs. (4a) and (4b). There the function $F(\mathbf{R}_{ij};\alpha,l;\beta,l')$ is associated with the matrix element coupling a basis state in which donor j is in its ground state and donor i is excited to the np state specified by α and located in valley l, to a basis state in which donor i is in its ground state and donor j is in the np state specified by β and located in valley l'. For simplicity the donor subscripts i and j will be dropped (R_{ij} will be written as R) and the components of $\mathbf{R}_{ij}$ will be written (X,Y,Z). (Note that for $i=j$ the matrix elements all vanish.) For Eq. (4a) (transitions to the np_0 states) one finds

$$F(1,1;1,1)=1-3X^2/R^2, \quad F(2,2;2,2)=1-3Y^2/R^2,$$

$$F(3,3;3,3)=1-3Z^2/R^2,$$

$$F(1,1;2,2)=-3XY/R^2,$$

$$F(1,1;3,3)=-3XZ/R^2, \quad F(2,2;3,3)=-3YZ/R^2.$$

For Eq. (4b) (transitions to the $np_\pm$ states) one has

$$F(2,1;2,1)=1-3Y^2/R^2, \quad F(3,1;3,1)=1-3Z^2/R^2,$$

$$F(1,2;1,2)=1-3X^2/R^2, \quad F(3,2;3,2)=1-3Z^2/R^2,$$

$$F(1,3;1,3)=1-3X^2/R^2, \quad F(2,3;2,3)=1-3Y^2/R^2,$$

$$F(2,1;3,1)=-3YZ/R^2,$$

$$F(1,2;3,2)=-3XZ/R^2,\quad F(1,3;2,3)=-3XY/R^2,$$

$$F(2,1;1,2)=-3XY/R^2\quad F(2,1;3,2)=-3YZ/R^2,$$

$$F(3,1;1,2)=-3XZ/R^2,$$

$$F(3,1;3,2)=1-3Z^2/R^2,$$

$$F(2,1;1,3)=-3XY/R^2,\quad F(2,1;2,3)=1-3Y^2/R^2,$$

$$F(3,1;1,3)=-3XZ/R^2,$$

$$F(3,1;2,3)=-3YZ/R^2,$$

$$F(1,2;1,3)=1-3X^2/R^2,\quad F(1,2;2,3)=-3XY/R^2,$$

$$F(3,2;1,3)=-3XZ/R^2,$$

$$F(3,2;2,3)=-3YZ/R^2.$$

These functions are symmetric in the sense that

$$F(\alpha,l;\beta,l')=F(\beta,l';\alpha,l).$$

Similar, albeit more complicated, expressions can be obtained for donors in Ge.

APPENDIX B

Envelope functions and pertinent matrix elements involving them for Eqs. (4a)–(4b) are discussed in this Appendix. Effective-mass envelope functions for a shallow-donor electron in Si are eigenfunctions of the problem

$$\left[-\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\gamma\frac{\partial^2}{\partial z^2}\right)-\frac{2}{r}\right]\psi=E\psi, \tag{B1}$$

where the electron is assumed to reside in the z valley [the conduction-band valley along (0, 0, 1)]. Here the notation and parameter values of Faulkner[10] are adopted, wherein $\gamma=m_\perp/m_\parallel=0.2079$, the energy is measured in units of the effective rydberg given by $\mathrm{Ry}=\hbar^2/2m_\perp a^2=e^2/2\epsilon_0 a=19.9\ \mathrm{meV}$, and $a=\epsilon_0\hbar^2/m_\perp e^2=3.17\ \mathrm{nm}$. Lengths in Eq. (B1) are in units of a and energy in units of rydberg. In these units, from Eqs. (6a) and (6b), one has

$$v_0=\frac{e^2}{\epsilon_0 a}(n_d a^3)|\langle 1s|z|np_z\rangle|^2/3=2\,\mathrm{Ry}(n_d a^3)|\langle 1s|z|np_z\rangle|^2/3, \tag{B2a}$$

$$v_\pm=\frac{e^2}{\epsilon_0 a}(n_d a^3)\langle 1s|x|np_x\rangle^2/3=2\,\mathrm{Ry}(n_d a^3)\langle 1s|x|np_x\rangle|^2/3. \tag{B2b}$$

Variational wave functions of the form proposed by Kohn and Luttinger are known to give very accurate energies for the lowest s-like and p-like levels of Eq. (B1) for $\gamma>0.2$. These wave functions have the following forms (not normalized):

$$1s:\quad \exp[-\kappa_s(x^2+y^2+\alpha_s z^2)^{1/2}],$$

$$2p_{x(y)}:\quad x(y)\exp[-\kappa_\pm(x^2+y^2+\alpha_\pm z^2)^{1/2}],$$

$$2p_z:\quad z\exp[-\kappa_z(x^2+y^2+\alpha_z z^2)^{1/2}],$$

where values of κ and α are determined variationally for each of these functions. When this is done and normalized functions are employed one obtains from effective-mass envelope functions

$$|\langle 1s|z|2p_z\rangle|^2=0.144, \tag{B3a}$$

$$\langle 1s|x|2p_x\rangle|^2=0.243. \tag{B3b}$$

It is well known that the effective-mass envelope functions give a very accurate description of the p states, but, for Si:P the ground state is much lower in energy than predicted by Eq. (B1). Thus the $1s$ envelope function, associated with the effective-mass theory ground-state energy, is certainly not at all accurate. To obtain a more accurate $1s$ wave function (away from the origin) one should insert the experimental ground-state energy on the right-hand side of Eq. (B1) and solve for the wave function. This is done in an approximate way to be described below. The results, using an experimental energy of -2.286 Ry for the ground state of P donors,[1] are

$$|\langle 1s|z|2p_z\rangle|^2=0.030, \tag{B4a}$$

$$\langle 1s|x|2p_x\rangle|^2=0.079. \tag{B4b}$$

The $1s$ wave function in Eqs. (B3a) and (B3b) is the effective-mass $1s$ state whereas that function has been modified to take into account central cell corrections in Eqs. (B4a) and (B4b). The values in Eqs. (B4a) and (B4b) are to be used in Eqs. (B2a) and (B2b) to obtain numerical values of v_0 and $v_\pm$ at donor concentrations of interest.

To find an approximate ground-state solution to Eq. (B1) with E replaced by the experimental ground-state energy E_{exp}, it is convenient to transform coordinates as in Ref. 8. Let

$$x'=x,\quad y'=y,\quad z'=\gamma^{-1/2}z.$$

In terms of the primed coordinates Eq. (B1) becomes

$$-\{\nabla^2+2/r[1+(\gamma-1)\cos^2\theta]^{-1/2}\}\chi=E_{\mathrm{exp}}\chi, \tag{B5}$$

where the primes have been omitted. The potential in Eq. (B5) is expanded in Legendre polynomials and all terms except the first are dropped. The resulting equation is one dimensional and has the form

$$-\left[\frac{1}{r}\frac{d^2}{dr^2}r+\frac{2V_0}{r}\right]f(r)=E_{\mathrm{exp}}f(r). \tag{B6}$$

where $f(r)$ is the required envelope function and

$$V_0=\int_0^1[1+(\gamma-1)\cos^2\theta]^{-1/2}d\cos\theta=1.233.$$

Let $g(2E_{\mathrm{exp}}^{1/2}r)/r=f(r)$. Substituting into Eq. (B6) leads to the equation

$$\frac{d^2}{dz^2}g(z)+(-1/4+\lambda/z)g(z)=0, \tag{B7}$$

where $z=2E_{\mathrm{exp}}^{1/2}r$ and $\lambda=V_0/\sqrt{|E_{\mathrm{exp}}|}$. Note that Eq. (B7) is Whittaker's equation, with the solution regular at infinity given in conventional notation by

$$g(z)=W_{\lambda,1/2}(z).$$

A useful integral representation for W is given by

$$W_{\lambda,1/2}(z)=\frac{z^{\lambda}\exp(-z/2)}{\Gamma(1-\lambda)}\int_0^{\infty}t^{-\lambda}(1+t/z)^{\lambda}e^{-t}dt.$$

where the gamma function is defined by

$$\Gamma(1-\lambda)=\int_0^{\infty}t^{-\lambda}e^{-t}dt.$$

In Ref. 8 higher terms are kept in the Legendre-polynomial expansion of the potential in Eq. (B5). It appears that this more nearly exact treatment leads to somewhat smaller values of the matrix elements than are reported here in Eqs. (B4a) and (B4b).

---

[1] C. Jagannath, Z. W. Grabowski, and A. K. Ramdas, Phys. Rev. B **23**, 2082 (1981).

[2] H. Navarro, E. E. Haller, and F. Keilmann, Phys. Rev. B **37**, 10 822 (1988).

[3] See, for example, M. Capizzi, G. A. Thomas, F. DeRosa, R. N. Bhatt, and T. M. Rice, Solid State Commun. **31**, 611 (1979).

[4] D. M. Larsen, *Proceedings of the International Conference on the Physics of Semiconductors*, Edinburgh, 1978, Conference Series No. 43, edited by B. L. H. Wilson (Institute of Physics, University of Reading, Berkeley, 1979), p. 529.

[5] D. M. Larsen and H. L. Fox, Phys. Rev. B **61**, 16 720 (2000).

[6] W. Kohn in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), p. 258.

[7] W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 352 (1955).

[8] Sh. M. Kogan and R. Taskinboev, Fiz. Tech. Poluprovodn. **17**, 1583 (1983) [Sov. Phys. Semicond. **17**, 1007 (1983)].

[9] Despite the coherence of the excited wave functions, phonon emission rates are the same as for excited isolated donors. If $M(k)$ is the matrix element for emission of a phonon with wave vector $\mathbf{k}$ from, say, an isolated donor in the $2p_0$ state to the ground state, then $|\Sigma_{i=1}^{N}\Sigma_{l=1}^{3}c_{i,l}(2p_0)M(k)\exp(-ik\cdot R_i)|^2$ is the squared matrix element for phonon emission from a coherent excited $2p_0$ state. ($\mathbf{R}_i$ is the position of the ith donor.) But this is equal to $M(k)^2\{\Sigma_{i\neq j}^{N}\Sigma_{l,l'=1}^{3}c_{i,l}(2p_0)\exp[-ik\cdot(\mathbf{R}_i-\mathbf{R}_j)]+\Sigma_{i=1}^{N}\Sigma_{l=1}^{3}|c_{i,l}|^2\}$. The first term on the right-hand side is the term arising from the coherent excitation and for an extended state should add to zero due to the random-phase factor given by the exponential. The second term adds up to 1 by normalization. As a result the squared matrix element is $M(k)^2$, which is the same as for an isolated excited donor.

[10] R. A. Faulkner, Phys. Rev. **184**, 713 (1969).