Excited states of the two-dimensional D^- center in magnetic fields

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Excited states of the two-dimensional D^- center (or H^- ion) are considered in the low-field and high-field limits. It is shown that in two dimensions there are no bound analogs of the large-radius bound excited states that spring into existence when an arbitrarily weak magnetic field is applied to a three-dimensional H^- ion. Asymptotically exact wave functions and energies are obtained in the limit of infinite magnetic field. In that limit, only four bound states are found in two dimensions: one spin singlet (symmetric space wave function), which is the ground state, and three spin triplets (antisymmetric space wave functions). It is pointed out that even those states that are unbound have, nevertheless, discrete energy levels in two dimensions (due to the Landau quantization of the planar motion) and play an essential role in the absorption of radiation by the D^- center. Connections between the two-dimensional D^- center and D^- centers in quantum wells are discussed.

I. INTRODUCTION

It is well known that a neutral hydrogen atom or a hydrogenic donor can bind a second electron to form a negative ion. In analogy to the terminology for hydrogen the donor ion formed in this way is called a D^- center. Simple hydrogenic D^- centers have been unambiguously identified in bulk samples of GaAs, a semiconductor in which shallow donors are very nearly hydrogenic, by means of the magnetic-field dependence of their photoionization threshold.[1] Recently reported experiments purporting to observe magneto-optical transitions associated with D^- centers in GaAs/(Ga,Al)As quantum wells[2] have motivated the present investigation of the excited states of these centers.

The importance of such excited states as final states in optical transitions originating from the ground state of the D^- does not seem to have been appreciated, although it turns out that in two dimensions and for quantum wells of experimentally interesting widths *photoionization* transitions to final states lying inside the quantum well do not occur; for photon energies too small to eject a D^- electron from the quantum well, all final states reached are discrete unbound states of the D^- center. The final states of interest cannot be expected to have energy separations from the ground state equal to the binding energy of the ground state, as has been assumed.[3] Thus the calculation of the optical-absorption frequencies of the D^- in a quantum well entails calculations not only of the ground-state energy[3] but also of energies of the appropriate excited states.

D^- states formed from a donor and a second electron confined to a common quantum well are always discrete because of the Landau quantization of the motion of electrons in the well planes and subband quantization of motion along the magnetic field (which is assumed perpendicular to the well planes in this paper). On the other hand, only some of these discrete states are bound in the sense that they lie lower in energy than the energy of the donor plus the energy of a free electron infinitely far from the donor and in the lowest Landau level. (In this paper the Zeeman spin energy of the D^- electrons is ignored; the spin state of the electrons affects the energies discussed only through the Pauli principle, which forces the overall electronic wave function to be antisymmetric.)

It is of interest to compare the physics of binding of D^- excited states in two dimensions to the three-dimensional binding. Remarkably, the three-dimensional H^- ion, which possesses only one bound state at zero magnetic field,[4] has an infinite number in any finite field.[5] To understand these excited bound states one must examine the potential produced by a hydrogen atom or a donor atom at distances r from the atomic center which are large compared to the Bohr radius, a, of the three-dimensional atom. This potential attracts negative charges toward the atomic center at all distances. It is proportional to[6]

$$|e|(1+r)e^{-2r}/r \ , \tag{1}$$

where, in Eq. (1) and elsewhere, the convention is adopted that all displacements are measured in units of a.

Although the attractive force associated with the potential of Eq. (1) decays exponentially with increasing r, the actual attraction of the atom on a distant electron is manyfold greater than implied by Eq. (1) because the attracting atom is polarized by the Coulomb field of the faraway electron. An atomic dipole moment, $\mathbf{p}$, is induced which points toward the electron. This dipole attracts the electron through its potential, p/r^2. The magnitude of p, being proportional to the electric-field strength from the distant electron evaluated at the atomic center, itself decreases with increasing r like $1/r^2$. Thus the attractive potential of the polarized atom is proportional to $1/r^4$ for large r. This potential binds the distant electron in the presence of weak magnetic fields.[5,7]

II. WEAK-FIELD LIMIT

For a two-dimensional donor or even a donor in the center of a quantum well the situation is completely

different. In both of these cases the charge distribution of the donor electron is not spherically symmetric as in three dimensions but, instead, is oblate. This oblateness arises, in quantum wells, from the squeezing of the donor wave function by the barriers and is associated with a buildup of electronic charge at the equator of the donor. The extra equatorial charge causes a repulsive contribution to the potential seen by a distant electron located in the same well as the donor.

More precisely, the atomic potential, $\Phi(\mathbf{r})$, evaluated at displacement $\mathbf{r}$ from the center of the unpolarized atom is given exactly by

$$|e|\Phi(\mathbf{r})=-2\int\frac{|\Psi(\rho',z')|^2}{|\mathbf{r}-\mathbf{r}'|}d^3r'+\frac{2}{r}\ , \tag{2}$$

where $\Psi(\rho',z')$ is the normalized ground-state wave function of the donor electron. Energies here and elsewhere are measured in units of the Rydberg, R, of the bulk donor. Taking the z direction perpendicular to the quantum-well planes, expanding in inverse powers of r, and noticing that for the unperturbed donor the monopole, dipole, and off-diagonal quadrupole moments vanish, one obtains the leading terms[8]

$$|e|\Phi(\mathbf{r})\sim\frac{Q(x^2+y^2)}{r^5}+\frac{Q_{zz}z^2}{r^5}\ , \tag{3}$$

where

$$Q=Q_{xx}=Q_{yy}=-\int(0.5\rho'^2-z'^2)|\Psi(\rho',z')|^2d^3r' \tag{4}$$

and $Q_{zz}=-2Q$. In Eq. (4), Ψ, the unpolarized donor ground-state wave function, is assumed to have cylindrical symmetry around z; the Q's are in units of $|e|a^2$. If $\rho^2>>L^2$, where L is the width of the quantum well ($L=0$ in the two-dimensional limit), then

$$|e|\Phi(\mathbf{r})\sim Q/\rho^3\ . \tag{5}$$

For oblate charge distributions, Q defined by Eq. (4) is negative; as a result the force associated with the potential given by Eq. (5) is repulsive for electrons. A comparison of the exact potential of Eq. (2) and the approximate potential of Eq. (5) is shown in Fig. 1 for the two-dimensional donor. The corresponding plot for the case of the donor and the distant electron in the middle of a quantum well would display a relatively weaker maximum, which is displaced to higher values of ρ. For quantum wells with $0.5<L<6$ and with infinitely high barriers variational calculations indicate that Q is greater than $\frac{3}{16}$, which is its value for the two-dimensional donor. (Calculations of Q for $L<0.5$ were not pursued.)

It is important to realize that at large ρ the potential of Eq. (5) dominates the dipole potential induced by the distant electron by virtue of the fact that the former decreases like $1/\rho^3$ whereas the latter falls off like $1/\rho^4$ as ρ gets very large. Thus the dipolar attraction is weaker than the quadrupolar repulsion at large distances and, in distinction to the situation in three dimensions, one cannot expect to find large-radius bound states of the D^- in weak magnetic fields.

One might ask whether there exist thresholds of magnetic field at which various excited D^- states in two dimensions do become bound and remain so at all higher fields. To answer this question in detail one might undertake a careful variational study of various D^- excited state energies as functions of magnetic field. (Results of a study of this sort will be reported elsewhere.) On the other hand, such states, if unbound at zero field, may be identified by investigating their binding in the strong-field limit. Obviously, a state which binds in this limit but which is unbound at zero field must have a threshold field.

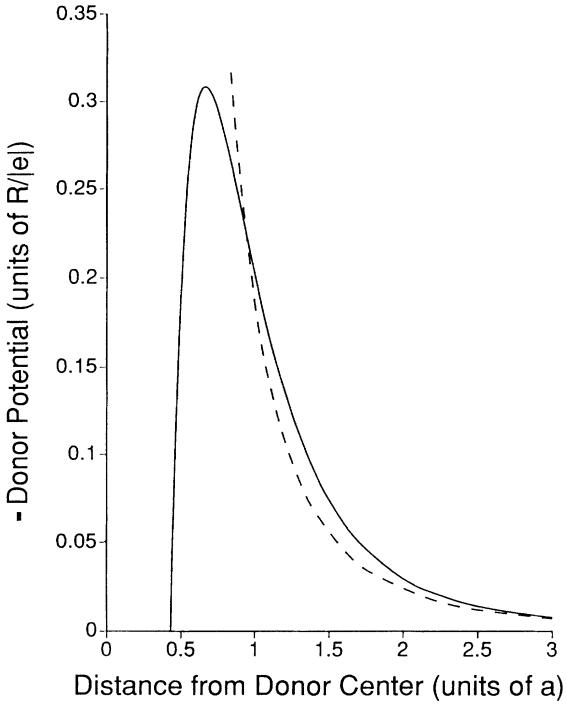

FIG. 1. Plot of the negative of the electrostatic potential due to the unperturbed two-dimensional donor atom in its ground state [$\Psi\approx\exp(-2\rho)$]. The solid line is the exact curve from Eq. (2), the dashed curved is the quadrupole potential from Eq. (5).

III. STRONG-FIELD LIMIT

In three-dimensional donor atomic units (energies in units of R, lengths in units of a) the Hamiltonian for an isolated D^- center in two dimensions has the form

$$H=H_D(1)+H_D(2)+2/|\boldsymbol{\rho}_1-\boldsymbol{\rho}_2|\ , \tag{6}$$

where $H_D(j)$ is the donor Hamiltonian for electron j ($j=1$ or 2) given by

$$H_0(j)=-\nabla_j^2+\frac{\gamma}{i}\frac{\partial}{\partial\phi_j}+\tfrac{1}{4}\gamma^2\rho_j^2\ , \tag{7}$$

$$H_D(j)=H_0(j)-\frac{2}{\rho_j}-\gamma\ ; \tag{8}$$

γ is the dimensionless magnetic-field strength defined by $\gamma=\hbar\omega_c/2R$, where $\omega_c=eB/mc$, B is the strength of the applied magnetic field, and m is the conduction-band

mass. Note from Eq. (8) that the zero of energy for the donor and the D^- is taken at the free-electron ground-state energy, γ, in the magnetic field.

The total Hamiltonian, H, is invariant under interchange of the indices 1 and 2 and under rotations about the z axis. Its eigenstates, therefore, may be classified according to (a) their total component of angular momentum in the z direction, labeled by the quantum number M, and (b) their symmetry (symmetric or antisymmetric) under interchange of coordinate indices 1 and 2.[9] The ground state of H is the $M=0$ symmetric state which, at zero magnetic field, has been calculated variationally by Phelps and Bajaj.[10]

By "strong-field limit" in two dimensions we mean here the limit $\gamma\to\infty$ in Eqs. (6)–(8).[11] It is easy to show that as $\gamma\to\infty$ the eigenfunctions of H can be expanded in linear combinations of products of pairs of one-electron ground-state eigenfunctions of Eq. (7), which individually have the form

$$X_M(\rho)=(\gamma^{1/2}\rho)^M\exp(-iM\phi)\exp(-\gamma\rho^2/4)\times\gamma^{1/2}/[2\pi(2M!!)]^{1/2}\ . \tag{9}$$

These (normalized) wave functions are defined for integer M from 0 to ∞; they are degenerate ground-state solutions of the free-electron problem

$$H_0X_M(\rho)=EX_M(\rho) \tag{10}$$

corresponding to z angular momentum $-M$ and energy $E=\gamma$. All other solutions to Eq. (10) have energies $(2N+1)\gamma$, where N, the Landau quantum number, is a positive integer greater than zero. Spacings between the ground-state levels and the excited levels are therefore of order γ, whereas all relevant matrix elements of the Coulomb potentials in H are easily shown to be only of order $\gamma^{1/2}$. As a result, admixtures of states with $N\geq 1$ can be neglected in the eigenstates of H or of H_D in lowest order, and D^- energies obtained are exact to order $\gamma^{1/2}$.

Each function in Eq. (9) is a donor eigenfunction to lowest order in the high-field limit because the Coulomb potential, $-2/\rho$, does not couple states of different M. The lowest-order neutral donor (D^0) energies are

$$E_D(M)=\langle X_M|H_D|X_M\rangle=\begin{cases}-(2\pi\gamma)^{1/2}\dfrac{(2M-1)!!}{(2M)!!} & (M>0)\\ -(2\pi\gamma)^{1/2} & (M=0)\ .\end{cases} \tag{11}$$

All other donor levels lie above the energies of Eq. (11) by an amount of order γ. Clearly $E_D(0)$ is the donor ground-state energy, as would be expected from Eq. (9), from which it is clear that the $M=0$ wave function is the most highly localized of the X_M's around $\rho=0$, the position of the positive charge.

D^- eigenfunctions in the high-field limit can be constructed from the basis functions

$$\Phi^{\pm}(M_1,M_2)=X_{M_1}(\rho_1)X_{M_2}(\rho_2)\pm X_{M_1}(\rho_2)X_{M_2}(\rho_1) \tag{12}$$

by taking linear combinations

$$\Psi^{\pm}(M)=\sum_{M_1=0}^{M}C(M_1,M-M_1)\Phi^{\pm}(M_1,M-M_1)\ , \tag{13}$$

where $-M$ is the total z angular momentum of the D^- state and the $+$ and $-$ superscripts refer to symmetric and antisymmetric (space) eigenstates, respectively. It is straightforward to solve the Schrödinger equation

$$H\Psi^{\pm}(M)=E^{\pm}(M)\Psi^{\pm}(M) \tag{14}$$

for the C's and eigenvalues $E^{\pm}(M)$ once the matrix elements of the repulsive potential in Eq. (6) between the various $\Phi^{\pm}$ functions have been obtained. These matrix elements have been calculated by numerical integration in this work. A list of the lowest eigenvalues for each of various symmetric and antisymmetric states is given in Table I. Also listed there is the corresponding second-electron binding energy, defined as the minimum energy required to remove *one* of the two D^- electrons to infinity. This quantity is positive only for bound D^- states. Binding occurs for the lowest-lying $M=0$ symmetric state and $M=1$, 2, and 3 antisymmetric states.

The eigenstate $\Psi^{\pm}(M)$ corresponding to each eigenvalue $E^{\pm}(M)$ appearing in Table I is either a pure $\Phi^{\pm}(M,0)$ state (as in the case of $M=1$ and 2 for antisymmetric states and $M=0$ and 1 for symmetric states) or else consists predominantly of that state. Notice that as M increases the energy differences $E^+(M)-E^-(M)$ quickly get smaller. This occurs because the exchange integrals occurring in matrix elements of $2/|\boldsymbol{\rho}_1-\boldsymbol{\rho}_2|$ diminish rapidly with increasing M as compared to the Coulomb integrals.

The spectrum of optical transitions from the ground state is particularly simple in the high-field limit. For light propagating along the magnetic field (normal to the two-dimensional plane) the dipole selection rule is $\Delta M=\pm 1$. In addition there is always the general selection rule that requires that the initial and final space states either be both symmetric or both antisymmetric. The ground state of the D^- is $\Psi^+(0)$. In the high-field

TABLE I. Energies $E^+(M)$ and $E^-(M)$ and corresponding second-electron binding energies $e_B^+(M)$ and $e_B^-(M)$ of the lowest-lying symmetric and antisymmetric state, respectively, of the two-dimensional D^- center with quantum number M. The energies are presented in units of $\gamma^{1/2}R$. The E values are measured relative to the lowest Landau level. Only states with positive e_B values are bound.

M	$E^+(M)$	$e_B^+(M)$	$E^-(M)$	$e_B^-(M)$
0	−3.2409	0.7343		
1	−1.9877	−0.5189	−2.873 7	0.3668
2	−2.4824	−0.0242	−2.560 4	0.0538
3	−2.4776	−0.0290	−2.508 55	0.0019
4	−2.4839	−0.0227	−2.495 4	−0.0112
5	−2.4873	−0.0193	−2.492 9	−0.0137
6	−2.4912	−0.0154	−2.493 5	−0.0131
7	−2.4937	−0.0129	−2.494 85	−0.0118
8	−2.4958	−0.0108	−2.496 3	−0.0103

limit this state has nonzero dipole matrix elements to only two states. One of these is $\Psi^+(1)$ with energy $E^+(1)$ given in Table I. The other is a replica of $\Psi^+(1)$ but with angular momentum equal to $+1$ (instead of -1) and with energy $E^+(1)+2\gamma$ (recall that 2γ is the cyclotron resonance transition energy in the present system of units).[12] Transitions occurring at the binding energy of the D^- ground state would require $\Delta M=\pm\infty$, as discussed below. Note that the transition energy for $\Psi^+(0)\rightarrow\Psi^+(1)$ is $\sim 21\%$ higher than the binding energy of the D^- ground state.

Both $E^+(M)$ and $E^-(M)$ appear from Table I to approach from above the threshold energy for binding, $-(2\pi)^{1/2}\sim -2.506\,628$, for large M. In fact, the discussion leading to Eq. (5) is applicable for analyzing the lowest-lying large-M wave functions $\Psi^{\pm}(M)$ in the strong-field limit and for showing that these wave functions, unbound at sufficiently large M, have energies which approach (from above) the threshold energy for binding as $M\rightarrow\infty$. The condition for applicability of Eq. (5) is that the second electron be, on average, much farther away from the positive ion than is the donor electron. This condition is well satisfied by the two-electron wave function $X_M(\rho_1)X_0(\rho_2)$ if M is sufficiently large, since the donor wave function $X_0(\rho_2)$ has a much smaller radius than the outer-electron wave function $X_M(\rho_1)$, which, moreover, vanishes rapidly at small ρ_1. From Eq. (5) one would infer that the energy of the two-electron wave function just introduced (more precisely, the expectation value of H in that wave function) lies above the D^- ionization energy by an amount proportional to

$$\langle X_M|\rho_1^{-3}|X_M\rangle\sim M^{-3/2}\ . \tag{15}$$

Since H is symmetric in electron indices, the energy of the state $X_M(\rho_2)X_0(\rho_1)$ is the same as that of $X_M(\rho_1)X_0(\rho_2)$. But since exchange terms are negligible at large M, $\Phi^{\pm}(M,0)$ must also have very nearly the same energy as these two product functions. Corrections to the energy of $\Phi^{\pm}(M,0)$ induced by admixing $\Phi^{\pm}(M-1,1)$ and other basis wave functions as prescribed by Eq. (13) can be shown to be of order M^{-2} and smaller. (The M^{-2} correction arises from polarization of the donor by the outer electron.) As a result the lowest D^- energy for a given M value and symmetry type (symmetric or antisymmetric) approaches the binding threshold from above as $M\rightarrow\infty$.

This conclusion is *not* expected to apply to D^- centers in quantum wells in the high-field limit (L fixed, $\gamma\rightarrow\infty$). At sufficiently high magnetic fields the donor ground state becomes prolate, producing an *attractive* quadrupole potential far from the donor center, which may well bind all states of sufficiently high M.

IV. SUMMARY AND CONCLUSIONS

It is shown that the D^- problem in a quantum well or in the two-dimensional limit differs in fundamental ways from the analogous problem in bulk. In two dimensions with a uniform magnetic field present all states, whether bound or unbound, are discrete. Excited states with $|M|\gg 1$ are expected to be unbound in the weak-magnetic-field limit, unlike the situation in bulk samples. In the high-field limit only four bound states have been found for the two-dimensional D^- although an infinite number are expected for D^- centers in quantum wells. The decisive role played by the donor quadrupole moment is emphasized. It is pointed out that in the two-dimensional high-field limit the two allowed optical transitions from the ground state both have substantially higher energies than the binding energy of the D^- center. There is no reason to expect that any of the allowed transition energies at intermediate fields are very close to the binding energy of the D^-.

Whether inserting the correct excited state energies into the calculations of Ref. 3 would bring the predicted transition energies into agreement with the experimental results of Ref. 2 is an issue that is currently under investigation.

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[8]See Ref. 6, p. 138.

[9]The Pauli principle requires that the spin wave function associated with the symmetric space state be antisymmetric (a spin singlet) whereas those associated with the antisymmetric space state be symmetric (spin triplet states).

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[11]The two-dimensional limit can be defined as the limit of a quantum well with infinitely high barriers as $L\rightarrow 0$. The strong-field limit in two dimensions referred to in this paper should be understood as the result of two limiting processes: first the limit $L\rightarrow 0$ is taken, followed by the limit $\gamma\rightarrow\infty$. The order of the limits is very important.

[12]In the dipole approximation the perturbation due to left circularly polarized light incident on the D^- center is proportional to $\rho\exp(-i\phi)$. This perturbation operating on $X_M(\rho)$ produces, to within a multiplicative constant, $X_{M+1}(\rho)$ [see Eq. (9)]. As a consequence, left-circularly-polarized light couples the high-field D^- ground state to the excited state $\Psi^+(1)$ and to no other state. Likewise right-circularly-polarized light, which leads to a term in the Hamiltonian proportional to $\rho\exp(i\phi)$, couples the high-field ground state to the state $\{\rho_1\exp(i\phi_1)\exp[-\gamma(\rho_1^2+\rho_2^2)/4]+1\leftrightarrow 2\}$ and to no other state.