Negative-Donor Centers in Semiconductors and Quantum Wells

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The negative-donor centers D^- in a magnetic field in semiconductors and quantum wells are studied by an effective-mass model which is solved exactly by a diffusion quantum Monte Carlo method. For D^- in bulk GaAs, excellent agreement is found between theory and magneto-optical experiments. For D^- in a 100-Å GaAs/$Ga_{0.75}Al_{0.25}As$ quantum well, a sevenfold increase in binding energy over that of the bulk case is predicted at zero field and the calculated field-dependent ground-state energy is in good agreement with the interpretation of recent high-field magneto-optical data.

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There is an increasing interest in the electronic structure and properties of donor centers in semiconductors and quantum wells in strong magnetic fields.[1-3] Many novel effects in these systems, such as quantum Hall effects, metal-insulator transitions, and electron localizations, are intimately related to phenomena of high magnetic fields and impurity states.[1]

A negative-donor center (D^-) in a semiconductor is formed by a neutral center (D^0) trapping an extra electron.[2] For homogeneous semiconductors, such as GaAs, InP, or InSb, states associated with D^- can be thought of as the states of two electrons of effective mass m^* under a central Coulomb potential screened by the dielectric constant.[1] This effective-mass model has been highly successful in discussing neutral shallow donors. However, because of the importance of electron-electron interactions, very accurate solutions for such a model of D^- centers in magnetic fields and quantum wells have not been available. For example, comparison[2] of experimental data of D^- states in bulk GaAs with previous theoretical results[4] showed that the experimental binding energies are systematically higher than the theoretical values, and the discrepancy increases with the applied magnetic-field strength. More recently, D^- states have been identified experimentally in selectively doped GaAs/$Ga_{0.75}Al_{0.25}As$ multiple-quantum-well structures with layer thickness of 100 Å for both compounds.[3] Magneto-optical measurements were carried out with an applied field perpendicular to the well structures. The results show that D^- centers are observable at fields larger than 4 T, and there is a strong enhancement of the binding energy of the D^- states in the quantum wells. However, there were no theoretical results available for the quantum-well systems.

In the present work, the effective-mass model is applied to the D^- and D^0 centers and the model is solved by a diffusion quantum Monte Carlo method[5,6] (DQMC) for cases with applied magnetic fields and in a quantum-well structure. The DQMC approach in principle provides the exact ground-state properties of the system apart from statistical noises. For the bulk case, comparison of the present work with the experimental data of D^- centers in GaAs shows excellent agreement, indicating that the model describes the system very well. The discrepancy[2] between the experimental data and previous variational results is identified and resolved.

For D^- centers in a quantum well and perpendicular magnetic fields, good agreement is also found with the data of Huant, Najda, and Etienne[3] in the high-field regime. At zero field and in a 100-Å GaAs/$Ga_{0.75}Al_{0.25}As$ quantum well, a surprisingly large enhancement of nearly sevenfold in binding energy as compared to the value of the bulk case is predicted. The effects of different effective masses and dielectric constants in the barrier and the well are found to be significant at zero field but become nearly negligible at very high field. (The high-field range is defined by $\gamma \geq 1$, where $\gamma = \hbar\omega_c/2R_y^*$ with ω_c the cyclotron frequency and R_y^* the effective Rydberg.) On the other hand, the effect of energy-dependent effective mass (arising from the nonparabolicity of the GaAs conduction band) is found to be important at high field.

For a D^- center located at the center of a single quantum well and with an applied field along the z direction, the Hamiltonian in the effective-mass model is given by

$$H = H(1) + H(2) + V(r_{12}) + (\gamma/2\eta)L_z , \quad (1)$$

with

$$H(i) = -\frac{1}{2\eta}\nabla_i^2 + \frac{\gamma^2}{8\eta}(x_i^2 + y_i^2) + U(r_i) + V_Q(z_i) , \quad (2)$$

where η is the ratio of the effective mass m^* in a specific region to that of bulk GaAs; γ is the magnetic field in the effective atomic units of GaAs; $V(r)$ and $U(r)$ are the interaction between two electrons and the interaction between an electron and the central charge, respectively, including all image charges due to the difference of the dielectric constants in the well, ϵ_1, and in the barrier, ϵ_2;[6,7] L_z is the angular momentum along the field direc-

tion; and $V_Q(z)$ is the quantum-well potential

$$V_Q(z)=\begin{cases}V_0, & |z|>d/2,\\ 0, & |z|\le d/2,\end{cases} \tag{3}$$

with V_0 the potential barrier height and d the well width. Only the $L_z=0$ case is considered here. Unless specified, the effective atomic units of GaAs with $m_0^*=0.067m_e$ and $\epsilon_0=12.53$ will be used for simplicity.

The binding energy of D^- can be written as

$$E_b=E_{D^0}+E_{Q\gamma}-E_{D^-}, \tag{4}$$

where E_{D^0} is the ground-state energy of D^0, $E_{Q\gamma}$ is the ground-state energy for a free electron in the quantum well $V_Q(z)$ and magnetic field γ, and E_{D^-} is the ground-state energy of Eq. (1). In order to obtain the exact ground-state energy of Eqs. (1) and (2), a quantum Monte Carlo method is chosen to simulate the Schrödinger equation as a diffusion equation of a time-dependent probability in configuration space.[5]

In the DQMC approach, one takes a variational wave function $\Phi(\mathbf{R})$ with $\mathbf{R}=(\mathbf{r}_1,\mathbf{r}_2)$ as a trial function for the ground state and constructs a time-dependent probability density $F(\mathbf{R},t)$:

$$F(\mathbf{R},t)=\Psi(\mathbf{R},t)\Phi(\mathbf{R}), \tag{5}$$

with

$$\Psi(\mathbf{R},t)=\exp\left[\int_0^t E_n(t')dt'-Ht\right]\Phi(\mathbf{R}), \tag{6}$$

where $E_n(t)$ is an as-yet-undetermined c number which can be considered as a normalization constant at the moment. As long as $\Phi(\mathbf{R})$ is not orthogonal to the exact ground state of H, $\Psi(\mathbf{R},t)$ will approach the ground state as t goes to infinity. Defining a time-dependent expectation value $E(t)$,

$$E(t)=\frac{\langle\Phi(\mathbf{R})|H|\Psi(\mathbf{R},t)\rangle}{\langle\Phi(\mathbf{R})|\Psi(\mathbf{R},t)\rangle}=\frac{\int d\mathbf{R}\,F(\mathbf{R},t)\epsilon(\mathbf{R})}{\int d\mathbf{R}\,F(\mathbf{R},t)}, \tag{7}$$

where $\epsilon(\mathbf{R})=\Phi^{-1}(\mathbf{R})H\Phi(\mathbf{R})$ is the local energy in configuration space, $E(t)$ becomes the exact ground-state energy of H as t goes to infinity.[5]

For the D^- center, since the ground state is a singlet of two electrons, the wave function has no node structure; that is, $F(\mathbf{R},t)$ is always positively defined. Therefore, Eq. (7) is equivalent to an average over a statistical weight $F(\mathbf{R},t)$:

$$E(t)=\frac{1}{M}\sum_i^M\epsilon(\mathbf{R}_i), \tag{8}$$

with $\mathbf{R}_i$ generated according to $F(\mathbf{R},t)$. In principle, $E(t)$ in Eq. (8) can be sampled by the Monte Carlo method exactly in the limit of zero time step interval. However, in practice, a zero time step interval is impossible. So the choice of the total simulation time and the time step interval is made by the accuracy required for the results. Generally, the statistical error of the Monte Carlo data is given by the total simulation time. The time step interval is chosen so that the error introduced will be within the statistical error of the data. The choice of the trial state $\Phi(\mathbf{R})$ will influence the speed of convergence of the results. Simulations with better trial states converge faster. The trial state used in this work has the form

$$\Phi(\mathbf{r}_1,\mathbf{r}_2)=f(r_{12})[g_1(r_1)g_2(r_2)+g_1(r_2)g_2(r_1)]\times\prod_{i=1}^{2}\phi(z_i)\kappa(\rho_i)w(r_i), \tag{9}$$

with $f(r)=\exp[ar/(1+br)]$, $g_i(r)=\exp[-c_ir^2/(d_i+e_ir)]$, $\phi(z)=\cos(kz)$ in the well and $\cos(kd/2)\times\exp[\lambda(d/2-|z|)]$ outside the well, $\kappa(\rho)=\exp(-\mu\rho^2)$, and $w(r)=\exp[\alpha r/(1+\beta r)]$. All the parameters a, b, c_i, d_i, e_i, k, λ, μ, α, and β are optimized by a variational Monte Carlo simulation first before Φ is used as a guide for the DQMC. Details on the variational parameters and the algorithm used in this work will be given elsewhere.[6]

Applying the method described above to the D^- centers, the ground-state energy can be obtained with very high accuracy. In Fig. 1, the present theoretical results together with results from two previous calculations using variational methods[4,8] are compared to the experimental results for the case of nominally undoped n-type GaAs.[2] It is clear that previous theoretical calculations have underestimated the binding energy compared to the DQMC result and are increasingly less accurate as the field strength increases. The excellent agreement of the present DQMC results with the experimental data indicates that the effective-mass model describes the D^- centers in GaAs very well. This result provides a definite answer to the important question asked in Ref. 2: What causes the discrepancy between the experimental data of

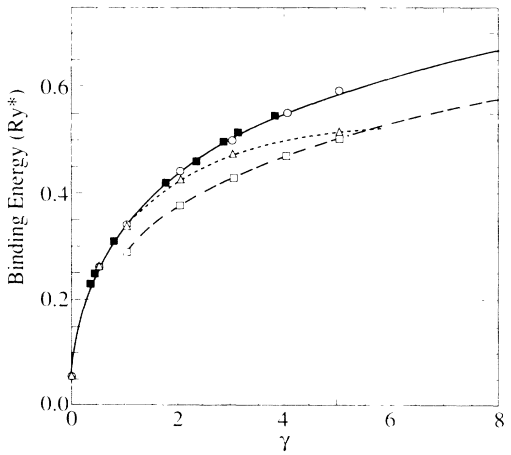

FIG. 1. Binding energies of D^- centers in GaAs from present work (○) compared with experimental data of Ref. 2 (■) and previous calculations of Ref. 8 (□) and Ref. 4 (△). The error bars of the present results are within the circles.

D^- in GaAs and the previous theoretical results for the model?[4,8] It was argued that central-cell and perhaps other crystal-field effects might be significant in this case, as they are in other systems, such as D^- centers in Si.[9] The present work shows that the discrepancy discussed in Ref. 2 is purely due to the inadequacy of the trial wave functions adopted in the previous calculations.

We have also calculated the electron-density distribution for the D^- center at different magnetic-field strengths.[6] In Fig. 2, the field dependences of the root-mean-square radius in the field direction, r_z, and that in the perpendicular direction, r_{xy}, are plotted. The competition between the electron-electron interaction and the attractive central potential leads to a configuration in which the two electrons in the system stay in two different orbitals in the zero-field case.[10] One is close to the $1s$ hydrogen atom orbital and the other is close to the $2s$ orbital. Under a strong magnetic field, the orbitals are pushed inwards in the x-y planes *as well as* in the z direction. From variational studies,[6,8] one finds that the second orbital gradually merges with the first orbital in increasingly high magnetic field.

From Fig. 1, it seems clear that the effective-mass model describes the D^- centers in a homogeneous GaAs compound very well provided that electron correlation is treated correctly. The same approach is applied to investigate D^- centers in the quantum-well structure formed by GaAs/$Ga_{1-x}Al_xAs$ heterojunctions. A recent experiment[3] has given evidence that the binding energies of D^- located around the center of the quantum well are strongly enhanced, although signatures for D^- states were only observed for $B>4$ T. In order to compare with the experimental data,[3] the experimental parameters for the quantum well in Ref. 3 are used to obtain the results summarized in Table I. The calculations were carried out in a single quantum well with well width 100 Å and Al concentration $x=0.25$. The barrier height is chosen as $0.65\Delta E_g$ with $\Delta E_g=1.247x$ eV as the gap

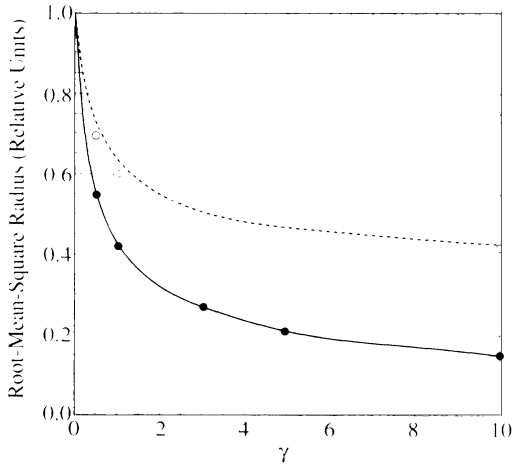

FIG. 2. The root-mean-square radius of D^- in GaAs in the field direction (○) and in the perpendicular direction (●).

TABLE I. Binding energy of D^- and D^0 centers in a GaAs/$Ga_{0.75}Al_{0.25}As$ quantum well. (a) $m_1=m_2$, $\epsilon_1=\epsilon_2$; (b) $m_1\neq m_2$, $\epsilon_1\neq\epsilon_2$; (c) same as (b) but with nonparabolicity of GaAs conduction band included (see text). Experimental data are from Ref. 3. Energy is in effective rydbergs of GaAs; $R_1^*=5.80$ meV. The Monte Carlo error bars are estimated at $0.02R_1^*$.

	Magnetic field $\gamma=\hbar\omega_c/2R_1^*$	Binding energy (R_1^*) Theory (a)	(b)	(c)	Expt.
D^-	0	0.29	0.33	0.35	···
	1	0.77	0.77	0.83	0.94
	3	1.13	1.11	1.22	1.28
D^0	0	2.09	2.16	2.23	···
	1	2.92	3.00	3.13	···
	3	3.89	3.94	4.18	···

mismatch between GaAs and $Ga_{1-x}Al_xAs$.[7] The effective mass and the dielectric constant in the well are chosen as those of bulk GaAs.

Two typical situations have been studied in detail: (1) The case with the effective mass m_2^* and dielectric constant ϵ_2 in the barrier the same as those in the well, and (2) the case with $m_2^*=(0.067+0.083x)m_e$ and $\epsilon_2=12.53-2.73x$.[7] The binding energies of D^- in these two cases are given in columns (a) and (b) in Table I. The corresponding results for D^0 are also given. It is necessary to include all the images of the central impurity charge and those of the electrons in the Hamiltonian in Eq. (1) when $\epsilon_1\neq\epsilon_2$.[6,7] When $m_1^*\neq m_2^*$, the boundary conditions $\Phi_1=\Phi_2$ and $m_2^*\,\partial\Phi_1/\partial z=m_1^*\,\partial\Phi_2/\partial z$ at the interfaces are imposed on the guiding wave function along the z direction.[7] The effect of the energy dependence of the effective mass[11] on the binding energy is also estimated by rescaling the results to an energy-dependent effective mass, and the modified results are given in column (c) in Table I. The energy-dependent effective mass is taken as

$$m^*(E)=(0.0665+0.0436E+0.236E^2-0.147E^3)m_e,$$

where E is the single-particle energy above the band edge in eV.[11] For the ground state of D^-, there is no well-defined single-particle energy. So half of the total energy is assigned to each electron in order to include this energy-dependent effect.

At zero magnetic field, the theory shows a dramatic increase, by a factor of 7, for the binding energy of D^- in the 100-Å quantum well as compared to that of the bulk case. The electron clouds in the quantum-well structure show that the electrons are further confined by the well potential.[6] Combined with the confinement due to the magnetic field, it leads to the strong enhancement of the binding energy of D^- in a quantum well. The theoretical results for the binding energy agree well with the experimental results at high fields where there are data. The calculated values are, however, about

(5–10)% lower than the experimental estimates.[3] Possible causes of the discrepancy may include enhanced central-cell effects in the well which are neglected in the theory or the effective well width which can be smaller than the layer thickness due to a nonsquarelike potential.

For the binding energies of the D^0 centers in quantum wells, since these are one-electron systems, the results of previous variational calculations are quite accurate.[7] For example, for a 100-Å $GaAs/Ga_{0.7}Al_{0.3}As$ well, Greene and Bajaj[12] obtained binding energies of $2.18R_y^*$ for $\gamma=0$ and $3.00R_y^*$ for $\gamma=1$, which are virtually identical with our results in column (b) in Table I.

We have also investigated the D^- centers in a 200-Å $GaAs/Ga_{0.75}Al_{0.25}As$ well. At $B=9$ T, or $\gamma=1.34$, the calculated D^- binding energy is significantly reduced from that of the 100-Å well to a value of 4.5 ± 0.1 meV which is in good agreement with the estimated value of 4.45 ± 0.25 meV from an analysis[13] of the experimental data of a 200-Å-well structure of $GaAs/Ga_{0.7}Al_{0.3}As$.[14] The actual details of the formation of the D^- centers in the quantum-well structures are, however, a complex matter. For the 100-Å well-width and barrier-width superlattice of $GaAs/Ga_{0.75}Al_{0.25}As$, the binding energy of the shallow donor (D^0) in the barrier center is found to be in fact slightly larger than the binding energy of the D^- centers in the well. The question of the mechanism for the source of the surplus electrons needed for the formation of the observed D^- centers for the samples used in Ref. 3 remains to be answered.

In conclusion, we have found that D^- states in bulk semiconductors such as nominally undoped n-type GaAs are well described by the effective-mass model. Comparing the present DQMC results with previous calculations shows that electron-correlation effects are very important in these systems and the simple trial wave functions adopted previously could not give a complete treatment of the correlation effects. However, the DQMC approach applied in the present work, in principle, has treated electron correlations exactly. For the D^- centers in quantum wells, the binding energy is in agreement with experimental data from multiple-quantum-well samples to within 10% after taking into account several important effects. The present theoretical results reinforce the identification made in Ref. 3 that the observed special feature in the spectra indeed arises from the ionization of D^- centers in the quantum well. The method used in this work may also be applied to the situation with the quantum well tilted relative to the magnetic field.

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