# Negative donors in bulk Si and Si/$SiO_2$ quantum wells in a magnetic field

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The spin-singlet ground states of a $D^-$ ion in bulk Si and Si/$SiO_2$ quantum wells have been investigated in the presence of a magnetic field, using a diffusion quantum Monte Carlo method. By neglecting the central-cell correction, the negative donor state can be assigned by the valley indexes of two trapped electrons. In the bulk Si, the ground-state energies of negative donors of both the intervalley and intravalley configurations split into two levels in a magnetic field along the $z$ axis and the lowest-energy state becomes the intervalley configuration of the two electrons in the valleys with their longitudinal axes perpendicular to the magnetic field. The magnetic field increases the binding energy of a negative donor and the strongest enhancement is attained for the intravalley configuration of the two electrons in the valley with the longitudinal axis parallel to the magnetic field. In the quantum well with the interface within the $x$-$y$ plane, the quantum confinement effect changes the lowest-energy state of a negative donor from the intervalley configuration in the bulk to the intravalley configuration for which the binding energy is increased most strongly by the magnetic field perpendicular to the well interface. The central-cell correction on the binding energy of a $D^-$ ion in a quantum well is also discussed.

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## I. INTRODUCTION

A neutral donor in the bulk semiconductors can bound weakly the second electron and this negative donor is called a $D^-$ ion. With respect to the $D^-$ state, a lot of theoretical studies have been performed by various methods, variational method,[1–3] diffusion quantum Monte Carlo (DQMC) method,[4] and full configuration-interaction approach;[5] but they have been applicable only to the single valley semiconductors with an isotropic effective mass. When the effective mass is isotropic, the magnetic-field dependence of the negative donor state has also been studied extensively.[4–7] In the presence of the magnetic field, it has been shown that there exist an infinite number of bound states for a $D^-$ ion,[8] while only one bound state exists in the absence of a magnetic field. Hujaj and Schmelcher[5] studied the lowest bound states of the hydrogen negative ions in the broad magnetic field regime. The global ground state is the spin-singlet state with the magnetic quantum number of $m=0$ in the weak field, but it is replaced by the spin-triplet state with $m=1$ because of the spin Zeeman effect. However, the binding energy of the spin-triplet state is much smaller than that of the spin-singlet state. For the $D^-$ ion in the bulk GaAs, the calculated field-dependent ground-state energy[4] for the spin-singlet state is in excellent agreement with the magneto-optical experiment.[9] It is shown that the spin-singlet state is the ground state for a magnetic field less than 80 T due to the low value of the $g$ factor in GaAs.[10] For a negative donor ion in a GaAs/$Ga_{0.75}Al_{0.25}As$ quantum well, a strong increase in the binding energy over that of the bulk is found and the calculated field-dependent ground-state energy[4,10] of the spin-singlet state is in good agreement with the high-field magneto-optical data.[11]

On the other hand, silicon is multivalley semiconductor and the minima of the conduction band are located in the vicinity of six equivalent $X$ points in the Brillouin zone. The effective mass parallel or perpendicular to the longitudinal axis in each valley becomes different and the multivalley semiconductors have anisotropic effective masses, contrary to the case of GaAs. The consideration to the anisotropy of the effective mass is essential to interpret the isolated donor states in Si. Faulkner[12] showed the anisotropic variational wave function for the donor state could give good results in the absence of the magnetic field. Mu *et al.*[13] extended the Faulkner's variational method to treat the donor state in the presence of the magnetic field. Kennedy and Kobe[14] proposed the gauge-invariant complex variational wave function for a shallow donor state in high magnetic fields.

As for an isolated $D^-$ ion in Si, extensive experimental studies were performed by Taniguchi and Narita[15] and it was pointed out that preparation of samples having very low impurity concentration and as small compensation as possible was very important. The concentration dependence of the $D^-$ state spectra indicates the transition from a shallow isolated $D^-$ state to a deeper bound state of an electron trapped by more than one neutral donor. The binding energies of the $D^-$ states in Si are determined to be 1.73, 2.05, and 1.75 meV for P, As, and Li impurities, respectively, in the stress free case.[16] Norton[17] obtained a similar value of 1.7 meV for both P and As impurities from the photoconductivity spectra at a low temperature. As for an interstitial Li impurity, the $D^-$ binding energy decreases linearly initially from 1.75 meV but suddenly changes to a constant value of 1.55 meV as the [100] stress increases. This transition was explained to be the change in the $D^-$ ground state induced by the uniaxial stress.[18] The observed 1.75 and 1.55 meV were assigned to the $D^-$ binding energies $\epsilon_{ij}$ of the intervalley and $\epsilon_{ii}$ of the intravalley configurations, respectively. Narita *et al.*[16] also studied the magnetic-field dependence of a negative donor state in Si. In the presence of the magnetic field along the [111] direction, the binding energies of the $D^-$ state increase

 

to about 3.32 and 2.95 meV at 6 T from 2.05 and 1.75 meV at zero field, for As- and Li-doped Si, respectively.

Very recently, meanwhile, a dopant has been expected as the functional part of a device instead of just providing charges. The electronic states of single dopants in gated silicon nanostructures have been studied through the transport spectroscopy, and the neutral $D^0$ and negatively charged $D^-$ states are observed by resonant tunneling between source and drain.[19] Furthermore, there has been a great deal of activity to develop a silicon-based quantum computer architecture such as direct exchange interaction[20] between electron spins in a donor, charge qubits[21] composed of two donors, and spin-to-charge transduction in donor-spin readout,[22] following the proposal by Kane.[23] In the entire spin-to-charge transduction process, measuring the state of the nuclear-spin qubit is turned into a spin-dependent electron charge-transfer event such as $D^0D^0 \rightarrow D^+D^-$ for a two-donor system.

In our previous paper,[24] we studied the multivalley effect on negative donors in multivalley semiconductors using a diffusion DQMC method under the condition that the central-cell correction for a donor ion can be neglected. We succeeded in producing well the experimental results for Si and Ge, in which the intravalley or the intervalley configuration is well controlled. For Si, we obtained $\epsilon_{ij}=1.82$ meV and $\epsilon_{ii}=1.57$ meV in good agreement with 1.75 and 1.55 meV for an interstitial Li impurity.[16] In the present paper, our purpose is to study the negative donors in both the bulk Si and $Si/SiO_2$ quantum wells in the presence of a magnetic field. We clarify both effects of the anisotropy of the effective mass and the multivalley structure, using the DQMC method. The binding energy of a negative donor is very small and hence the correlation effect between two trapped electrons is essentially important. To treat the correlation effect accurately, we used the DQMC method with the importance sampling.[25]

## II. CALCULATION METHOD

If the central-cell correction of a donor is neglected, each electron of a negative donor in Si belongs to a specific valley among the six equivalent valleys. Therefore, electron configuration of a $D^-$ ion is assigned by their valley indexes.[26] We call the configuration as $(i,i)$ intravalley when the two trapped electrons belong to the same valley $(i)$ and as $(i,j)$ intervalley when the two electrons belong to different valleys $(i)$ and $(j)$. In the effective-mass approximation, the Hamiltonian for a $D^-$ ion with the (1,1)-intravalley configuration in the presence of a magnetic field parallel to the $z$ axis is given by (see Fig. 1)

$$H(\boldsymbol{r}_1,\boldsymbol{r}_2) = H_1(\boldsymbol{r}_1) + H_1(\boldsymbol{r}_2) + \frac{1}{r_{12}},$$

$$H_1(\boldsymbol{r}_n) = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2}\right) - \frac{1}{2M_r}\left(\frac{\partial^2}{\partial z_n^2}\right) - \frac{1}{r_n} + \frac{\gamma^2}{8}(x^2+y^2) + \frac{\gamma}{2}L_z + V(z). \quad (1)$$

Here, $r_{12}$ is the distance between two trapped electrons,

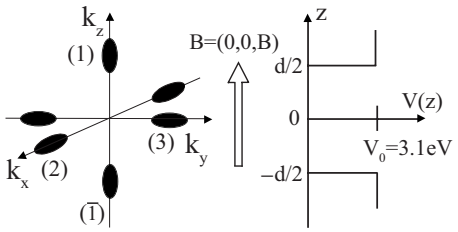


FIG. 1. The schematic figure of a $Si/SiO_2$ quantum well in the magnetic field along the $z$ direction and the equal energy surfaces in the vicinity of the conduction-band minimum of the bulk Si.

$H_1(\boldsymbol{r}_n)$ is the single-electron Hamiltonian for a neutral donor $D^0$ and $L_z$ represents the $z$ component of the angular-momentum operator. $\gamma$ is defined as $\gamma=\hbar\omega_c/\mathrm{Ha}^*$, using the cyclotron frequency $\omega_c=eB/m_t^*$. $V(z)$ is the square-well potential of a quantum well. We assumed a $Si/SiO_2$ quantum well in the $z$ direction and a donor was located at the center of the well. As for the well depth, we adopted 3.1 eV of the band offset between Si and $SiO_2$. $M_r$ in Eq. (1) is the ratio of the longitudinal effective mass $m_l^*$ to the transverse effective mass $m_t^*$ defined as $M_r=m_l^*/m_t^*$. Similarly, the single-electron Hamiltonian for an electron in the valley (3) can be written as

$$H_1(\boldsymbol{r}_n) = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial z_n^2}\right) - \frac{1}{2M_r}\left(\frac{\partial^2}{\partial y_n^2}\right) - \frac{1}{r_n} + \frac{\gamma^2}{8}\left(y^2 + \frac{x^2}{M_r}\right) + \frac{\gamma}{2}\left(\frac{p_y x}{M_r} - p_x y\right) + V(z). \quad (2)$$

In the above single-electron Hamiltonians (1) and (2), both differences of the effective masses and the dielectric constants between Si and $SiO_2$ were not considered. In Eqs. (1) and (2), the energy and the length are measured in the effective atomic units of $\mathrm{Ha}^*=m_t^*e^4/(4\epsilon^2h^2)$ and $a_B^*=\epsilon h^2/(\pi m_t^* e^2)$, respectively. For Si, $\mathrm{Ha}^*=35.4$ meV, $a_B^*=3.36$ nm, and $M_r=4.81$.[27] As for the strength of the magnetic field $B$, $\gamma=0.172$ at $B=10$ T.

The binding energy of a $D^-$ ion is calculated as

$$E_B^{D^-} = E_{D^0} + E_{\mathrm{free}} - E_{D^-}, \quad (3)$$

where $E_{D^0}$, $E_{\mathrm{free}}$, and $E_{D^-}$ are the ground-state energies of a neutral donor $D^0$, the free electron, and a negative donor $D^-$, respectively.

We used a DQMC method with an importance sampling[25] to calculate the ground-state energies $E_{D^0}$ and $E_{D^-}$. In DQMC method, a diffusion constant in each direction is inversely proportional to the corresponding effective mass of each electron. Hence, DQMC method can incorporate easily both the anisotropy effect of the effective mass and the multivalley structure into the computer program code.

We adopted the following simple trial functions for the $D^0$ state which traps an electron in the valley (1), in the importance sampling,

$$\psi_{D^0}^{\mathrm{tr}} = \exp\left(-\sqrt{\frac{x^2+y^2}{a_1^2}+\frac{z^2}{b_1^2}}\right). \quad (4)$$

In Eq. (1), $L_z$ commutes with the Hamiltonian $H_1$ and the eigenstate can be assigned by the magnetic quantum number $m$. The trial function of Eq. (4) has the magnetic quantum number of $m=0$. With respect to the trial function for the $D^0$ state which traps an electron in the valley (3), on the other hand, the magnetic quantum number $m$ cannot be taken as the good quantum number. For the free-electron state in the valley (3), the operator $L_z'=\frac{p_y x}{M_r}-p_x y$ commutes with the Hamiltonian and the eigenvalue $m'$ becomes the good quantum number. However, $L_z'$ does not commute with the Coulomb attractive interaction, i.e., $L_z'$ does not commute with the Hamiltonian of Eq. (2) as well as $L_z$. The attractive Coulomb interaction mixes the states with different values of $m'$ and the resultant wave function of the donor ground state becomes a complex function in a magnetic field,[13,14] instead of a real function at zero magnetic field. To treat the complex wave function in the DQMC method, we must use a fixed phase approximation.[28] In this paper, we assumed the following real trial function for the $D^0$ state trapping an electron in the valley (3) in the importance sampling:

$$\psi_{D^0}^{\mathrm{tr}} = \exp\left(-\sqrt{\frac{x^2}{a_3^2}+\frac{y^2}{b_3^2}+\frac{z^2}{c_3^2}}\right). \quad (5)$$

Assumption of the real trial function is equivalent to the neglect of the fifth term proportional to $L_z'$ in the Hamiltonian of Eq. (2) and hence the calculated energy gives the upper bound for the true ground-state energy.

We assumed the spin-singlet ground state for the $D^-$ state, since the spin-singlet state has the largest binding energy.[5] As for the trial function for the $D^-$ state, we adopted the direct product form of the donor wave function for each electron. $a_i$, $b_i$, and $c_i$ in Eqs. (4) and (5) are the variational parameters related to the extension of the wave function in each direction. The values of parameters are determined by optimization with a variational Monte Carlo (VMC) simulation.

## III. NUMERICAL RESULTS

### A. Bulk

At first, we show in Figs. 2(a) and 2(b) both the ground-state energies and the binding energies of a neutral donor in the bulk Si as a function of the magnetic field applied parallel to the $z$ direction. In calculation of the binding energy, the valley index of an electron was assumed to be conserved in the transition. The ground-state energies of the free electron in a magnetic field are given by the lowest Landau levels $\gamma/2$ and $\gamma/(2\sqrt{M_r})$ for the electron in the valleys (1) and (2), respectively. The ground-state energy of a neutral donor splits in the magnetic field similarly to the free electron and the electron in the valley (2) takes a lower energy than that in the valley (1). As for the binding energy, the electron in the valley (1) has a larger value because of its much higher lowest Landau level. Indeed, the increase in the binding energy is well approximated by $\gamma/2$ or $\gamma/2\sqrt{M_r}$ in the low field of $\gamma<0.2$ for the electron in the valley (1) or (2), respectively.

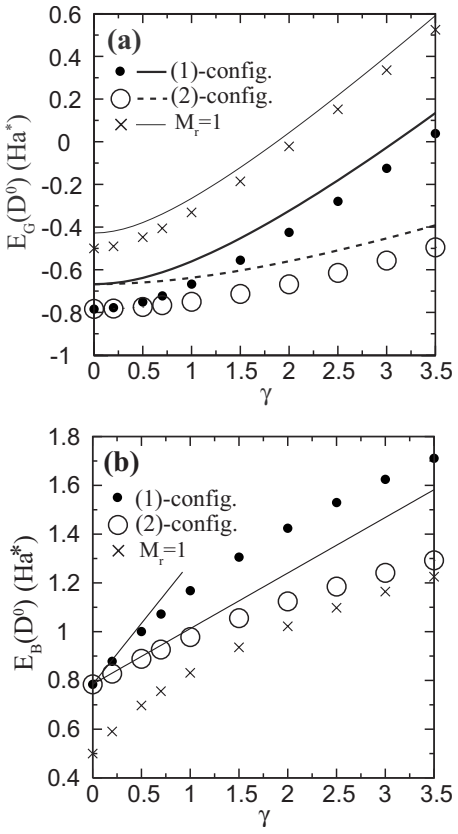


FIG. 2. (a) Ground-state energies $E_G(D^0)$ of a neutral donor with those calculated by the gauge-invariant variational method (Ref. 14) (three lines) and (b) the binding energies $E_B(D^0)$ as a function of the magnetic-field strength $\gamma$, with those for an isotropic effective mass of $M_r=1$. Two solid lines in (b) represent the relations of $\frac{\gamma}{2}+c$ and $\frac{\gamma}{2\sqrt{M_r}}+c$, respectively, where $c$ is $E_B(D^0)$ at $\gamma=0$.

In Fig. 2, the calculated result for the isotropic effective mass of $M_r=1$ is also plotted for comparison. In Fig. 2(a), the ground-state energies of a neutral donor calculated by the gauge-invariant variational method proposed by Kennedy and Kobe[14] are also drawn by three lines. Our DQMC method can give the exact ground-state energies of a neutral donor in a magnetic field for both cases of $M_r=1$ and the valley (1) electron configuration. For the valley (2) electron configuration, however, we can calculate the exact ground-state energy only at zero field and give the upper bound with decreasing accuracy as the magnetic-field strength increases. On the contrary, the variational wave function proposed by Kennedy and Kobe[14] gives good results in high fields. Our results in Fig. 2(a) always take lower energies than those obtained by the gauge-invariant variational method. This means that our calculation gives better results also for the valley (2) configuration than the gauge-invariant variational method in the studied magnetic-field range.

Next, we show in Figs. 3(a) and 3(b) both the energy levels of the ground states of a negative donor in the bulk Si and their binding energies as a function of the magnetic field applied parallel to the $z$ direction. In calculation of the binding energy, we assumed that the valley indexes of the two electrons are conserved in the transition. As for the one-electron excited state in the intervalley configuration, we

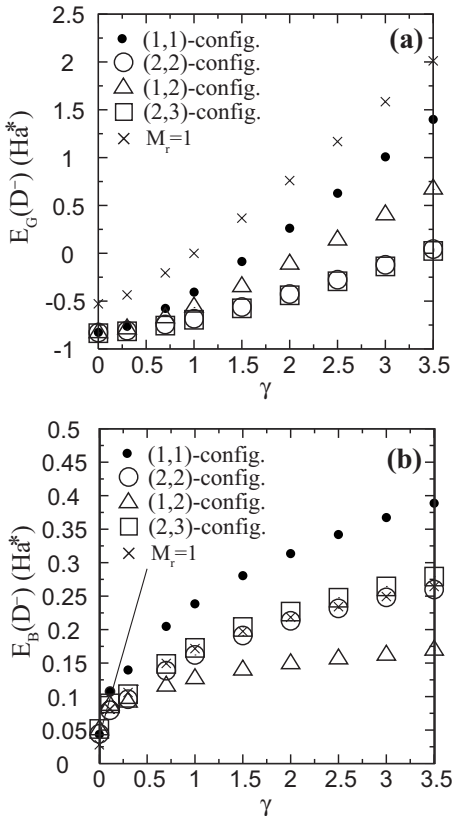


FIG. 3. (a) Ground-state energies $E_G(D^-)$ of a negative donor and (b) the binding energies $E_B(D^-)$ as a function of the magnetic-field strength $\gamma$, with those for an isotropic effective mass of $M_r=1$. The solid line represents the relation of $\frac{\gamma}{2}+c$, where $c$ is $E_B(D^-)$ at $\gamma=0$ for the (1,1)-intravalley configuration.

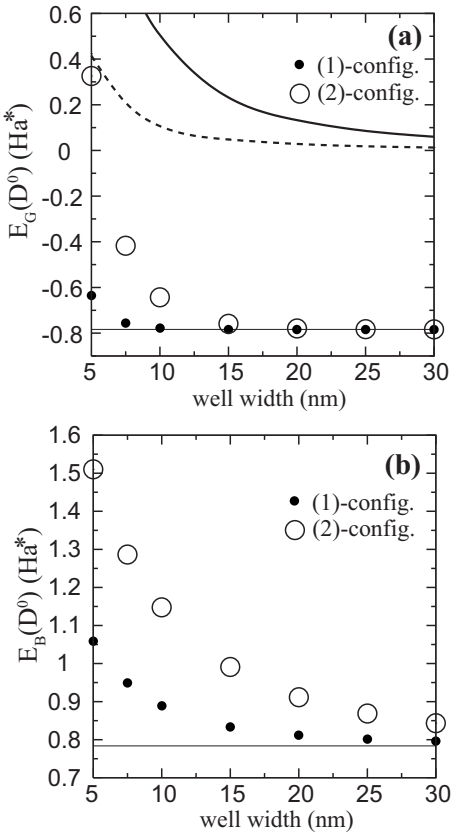


FIG. 4. (a) Ground-state energies $E_G(D^0)$ of a neutral donor in the $Si/SiO_2$ quantum well and (b) the binding energies $E_B(D^0)$ as a function of the well width, with the lowest free-electron levels for both the valley (1) electron (thick broken line) and the valley (2) electron (thick solid line). Here, $E_G(D^0)$ and $E_B(D^0)$ in the bulk are indicated by thin solid lines.

adopted the lower-energy configuration. In the magnetic field, there exist four kinds of electron configurations for the negative donor. The energy levels for both the intravalley and the intervalley configurations split into two levels by the magnetic field. The lowest (highest)-energy state of the negative donor is the (2,3)-intervalley [(1,1)-intravalley] configuration in the magnetic field. As for the binding energy of a negative donor ion, the magnetic field increases the binding energies. The magnetic-field effect is the largest for the (1,1)-intravalley configuration and the binding energy increases as $\gamma/2$ at low fields as shown in Fig. 3(b). The (2,3)-intervalley configuration has not so large magnetic-field effect and the binding energy increases as $\gamma/(2\sqrt{M_r})$ at low fields. In Fig. 3, the result for $M_r=1$ is also plotted for comparison. As for the ground-state energy of a negative donor for the isotropic effective mass, it must be larger than those in the bulk Si in which the longitudinal kinetic energy is suppressed, as seen in Fig. 3(a). The calculated $D^-$ binding energy for the case of the isotropic effective mass agrees well with the results by Pang and Louie.[4] The magnetic-field-induced increase in the $D^-$-binding energy is much more remarkable than the $D^0$-binding energy.

### B. Quantum well

At first, we study the well-width dependence of both a neutral donor and a negative donor in the absence of a magnetic field. We show in Figs. 4(a) and 4(b) both the energy levels of the ground states of a neutral donor in a quantum well and their binding energies as a function of the well width. In Fig. 4(a), the lowest energy of the free-electron state in the quantum well is also plotted. For the free-electron state in the valley (2) electron, the quantum confinement effect is already prominent at the well width of 30 nm. The ground-state energy of a neutral donor is affected by the quantum confinement effect for the well width less than about 15 nm and is increased compared to the bulk value. For the neutral donor in the well, the valley (1) electron takes the lower energy than the valley (2) electron similarly to the free electron; but their energy difference is much smaller than that of the free electron. With respect to the binding energy of a neutral donor in the well, it is strongly increased as the well width decreases. The enlargement can be seen already at the well width of 30 nm for the valley (2) electron.

Second, we show in Figs. 5(a) and 5(b) both the energy levels of the ground states of a negative donor in a quantum well and their binding energies as a function of the well width for the four kinds of electron configurations. The quantum confinement effect on a negative donor appears for the well width less than about 20 nm. In such a narrow quantum well, the electron configuration of the ground state of a negative donor changes to the (1,1)-intravalley configuration

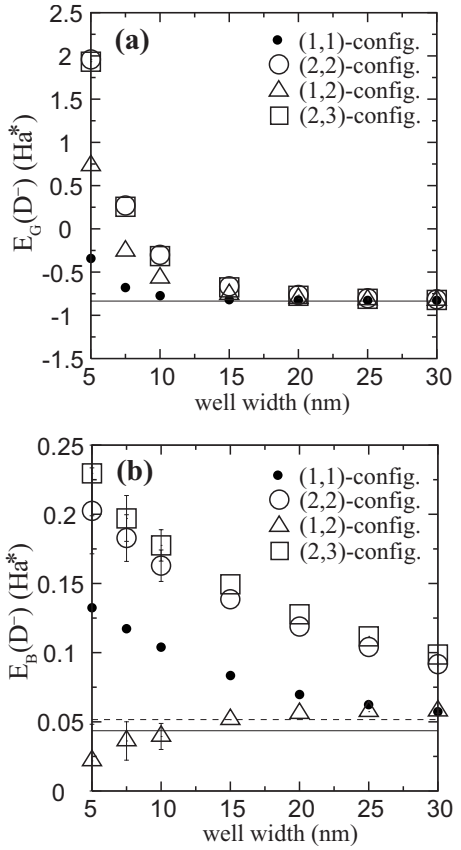


FIG. 5. (a) Ground-state energies $E_G(D^-)$ of a negative donor in the $Si/SiO_2$ quantum well and (b) the binding energies $E_B(D^-)$ as a function of the well width, with their bulk values [$\epsilon_{ii}$: solid line and $\epsilon_{ij}$: broken line. The two bulk values for $E_G(D^-)$ cannot be discriminated in this energy scale.]

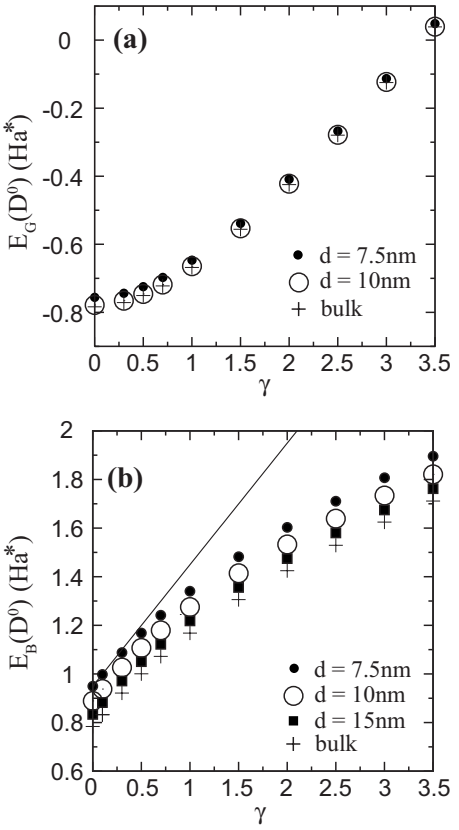


FIG. 6. (a) Ground-state energy $E_G(D^0)$ of a neutral donor for the (1)-valley configuration in the $Si/SiO_2$ quantum well and (b) the binding energy $E_B(D^0)$, as a function of the magnetic-field strength $\gamma$, with those in the bulk Si. The solid line represents the relation of $\frac{\gamma}{2}+c$, where $c$ is $E_B(D^0)$ at $\gamma=0$ for the well with $d=7.5$ nm.

from the intervalley configuration in the bulk. The binding energy of the $D^-$ ion increases as the well width decreases except one for the (1,2)-intervalley configuration. The behavior for the (1,2)-intervalley configuration means that a neutral donor which traps the valley (2) electron binds the valley (1) free electron more loosely as the well width decreases. This is induced by the enhanced repulsive Coulomb interaction between two trapped electrons in a negative donor in a narrower quantum well.

Third, we study the magnetic-field dependence of the ground states of a neutral donor and a negative donor in quantum wells with widths of 7.5, 10, and 15 nm. For these well widths, the quantum confinement effect affects strongly on their binding energies. We show in Figs. 6(a) and 6(b) both the ground-state energies and the binding energies of a neutral donor in the quantum well for the valley (1) electron with their bulk values, as a function of the magnetic field applied parallel to the $z$ direction. The enlargement of the binding energy of the neutral-donor ground state by both the well-confinement effect and the magnetic field can be seen in Fig. 6(b). It should be mentioned that the ground-state energy of a neutral donor $E_G(D^0)$ increases in proportion to $\gamma^2$ caused by the diamagnetic effect, but the binding energy $E_B(D^0)$ increases as $\gamma/2$ in the weak field caused by the ascent of the lowest Landau level.

Finally, we show in Figs. 7(a) and 7(b) both the ground-state energies and the binding energies of a negative donor with the (1,1)-intravalley configuration in the quantum well, as a function of the magnetic field applied parallel to the $z$ direction. The strong increase in the binding energy of the negative donor ground state by both the well-confinement effect and the magnetic field can be seen in Fig. 7(b). It is remarked that the ground-state energy of a $D^-$ ion $E_G(D^-)$ increases in proportion to $\gamma^2$ caused by the diamagnetic effect, but the binding energy $E_B(D^-)$ increases as $\gamma/2$ caused by the ascent of the lowest Landau level in the weak field of $\gamma<0.2$.

## IV. DISCUSSION AND CONCLUSION

The magnetic field increases both binding energies of a neutral donor and a negative donor. This is caused by the increase in the contribution of an attractive donor-ion potential resulting from suppression of the transverse extension of their electron orbits. In high fields of $\gamma \gg 1$, the transverse extension is reduced to the cyclotron radius $l$ of $l=a_B^*/\sqrt{\gamma}$. In Fig. 8, we plot the ratio $R$ of the binding energy of a negative donor with the (1,1)-intravalley configuration to the binding energy of a neutral donor with the (1)-valley configuration, as a function of the magnetic-field strength $\gamma$ for both the

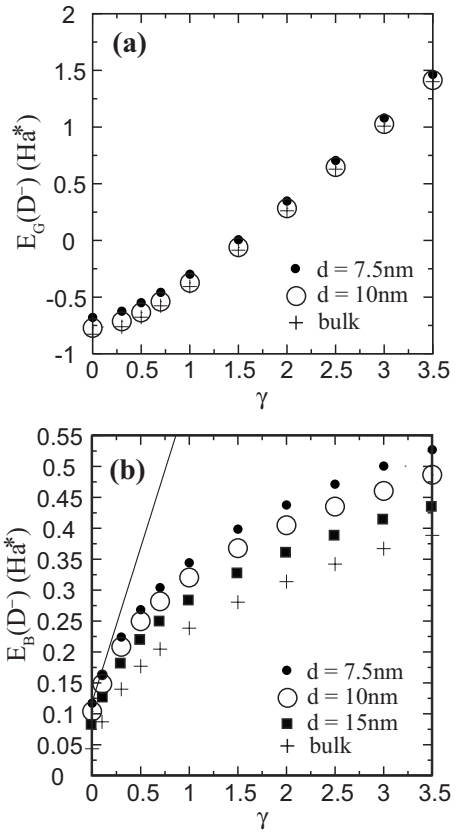


FIG. 7. (a) Ground-state energy $E_G(D^-)$ of a negative donor for the (1,1)-intravalley configuration in the $Si/SiO_2$ quantum well and (b) the binding energy $E_B(D^-)$, as a function of the magnetic-field strength $\gamma$, with those in the bulk Si. The solid line represents the relation of $\frac{\gamma}{2}+c$, where $c$ is $E_B(D^-)$ at $\gamma=0$ for the well with $d=7.5$ nm.

bulk Si and the $Si/SiO_2$ quantum well along the $z$ direction. It can be seen that the ratio $R$ initially increases linearly with increasing $\gamma$ and approaches to a constant value much larger

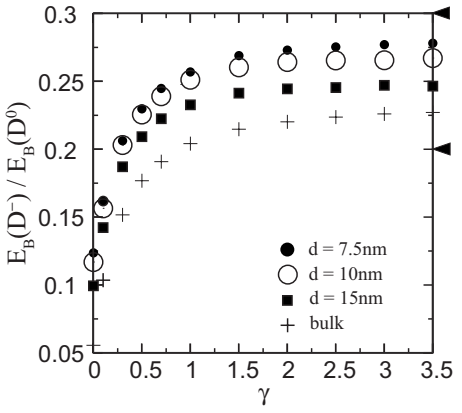


FIG. 8. The ratio of the $D^-$-binding energy $E_B(D^-)$ of the (1,1)-intravalley configuration to the $D^0$-binding energy $E_B(D^0)$ of the (1)-valley configuration in the $Si/SiO_2$ quantum well as a function of the magnetic-field strength $\gamma$, with those in the bulk Si. Two limiting values of 0.3 and 0.2 for two- and three-dimensional electron gas with an isotropic effective mass are indicated by two arrow heads.

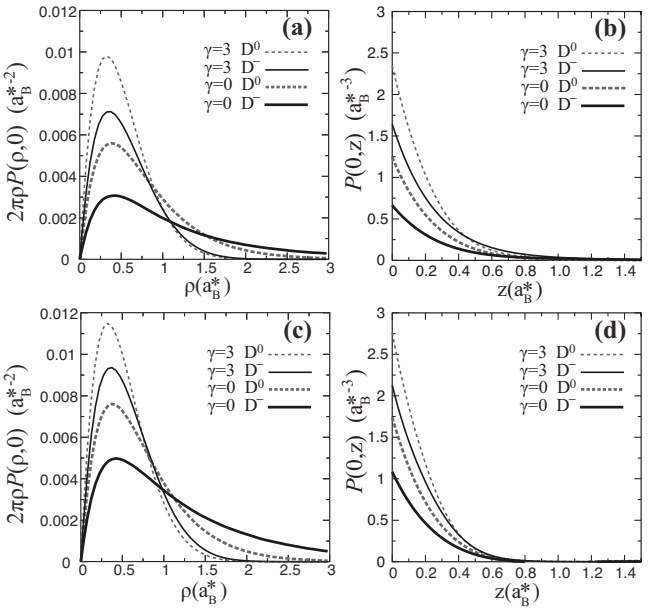


FIG. 9. The single-electron probability density $P(\rho,z)$ of a neutral donor for the (1)-valley configuration and a $D^-$ ion for the (1,1)-intravalley configuration in the bulk [(a) and (b)] and in a $Si/SiO_2$ quantum well with a width of 5 nm [(c) and (d)] at $\gamma=0$ and $\gamma=3$. Here, $\rho$ is the transverse direction and $z$ is the longitudinal direction parallel to the well direction.

than 0.055 in the bulk in the absence of a magnetic field. This ratio $R$ is insensitive to the anisotropy of the effective mass in the range of $1 \leq M_r < 10$ in the absence of the magnetic field in the bulk Si; although either value of $E_B(D^-)$ or $E_B(D^0)$ is increased with increasing the longitudinal effective mass, as mentioned in our previous paper.[24] The value of $R$ in the bulk with an isotropic effective mass is obtained as 0.21, 0.20, and 0.20 at $\gamma=10$, 100, and 1000 from a full configuration-interaction approach.[5] These values are a little smaller than the calculated asymptotic value in the bulk Si in Fig. 8. The value $R$ in the two-dimensional electron system with an isotropic effective mass, on the other hand, can be obtained as 0.30 at $\gamma=10$, 100, and 1000 from a finite-difference solution.[29] This value is a little larger than the calculated asymptotic value at the well width of 7.5 nm in Fig. 8. Calculated asymptotic values of $R$ are just located between these two limiting values of 0.2 and 0.3 for the three- and two-dimensional electrons with an isotropic effective mass. The increase of $R$ means that the electron-electron Coulomb interaction energy in a $D^-$ ion is reduced relatively to $E_B(D^0)$. This is caused by the increase in the electron correlation effect on two electrons in a negative donor and it is enhanced as the effective dimension is lowered. Indeed, the ratio $R$ is increased as the well width decreases by approaching to the two-dimensional system and is also increased with increasing $\gamma$ by approaching to the quasi-one-dimension in high fields.

Next, we discuss the effect of the magnetic field on the probability density of electrons. In Fig. 9, we present the single-electron probability densities of both a neutral donor for the (1)-valley configuration and a $D^-$ ion for the (1,1)-intravalley configuration in the bulk Si and in the quantum

well with a width of 5 nm. The magnetic field shrinks mainly the transverse extension of the probability density by the diamagnetic effect but the longitudinal extension is also reduced. This is caused by relative increase in the contribution of the attractive potential of a donor ion. The effect is more enhanced for a $D^-$ ion than for a neutral donor and the effect is suppressed in the quantum well compared to in the bulk. This is attributed to the enhancement of the diamagnetic effect on the state with a larger transverse extension. In the quantum well, the well-confining potential reduces also the transverse extension of the probability density in addition to the reduction in the longitudinal extension, as seen in Fig. 9.

Now, we discuss the central-cell correction on the potential of a donor ion in the effective-mass approximation. The central-cell correction is the short-range attractive interaction and the states assigned to each valley are mixed. The ground state of a neutral donor can be expressed as a linear combination of each valley state according to the symmetry. For a substitutional impurity, such as P and As in the bulk Si, the ground state of a neutral donor can be obtained as a linear combination of each valley state with an equal weight in the bulk and the energy is lowered by $6\Delta_c$ from the value obtained in the effective-mass approximation.[18] The ground state of a $D^-$ ion consists of two electrons with $A_1$ symmetry[18,26,30] and it can be written as the linear combination of the intravalley and the intervalley configurations. If the central-cell correction for the $D^-$ ion and the $D^0$ ground states are assumed to be the same, the $D^-$ binding energy can be simply approximated as[24,31]

$$E_B^{D^-} = [\epsilon_{ii} + (g-1)\epsilon_{ij}]/g. \tag{6}$$

Here, $g$ is related to the valley degeneracy and $g$ takes three for the bulk Si. On the other hand for an interstitial Li impurity in the bulk Si, the ground state of a neutral donor has $T_1$ symmetry and the effect of the central-cell correction is diminished for the binding energy.[18] The $D^-$ ground state consists of two electrons with $T_1$ symmetry and its binding energy can be reduced to that of the intervalley configuration $\epsilon_{ij}$ in the bulk.[18]

Here, we consider the central-cell correction for both a neutral donor and a $D^-$ ion in a narrow quantum well along the [001]-direction, where the valley degeneracy is two. If we assume the short-range potential of the central-cell correction as a delta function $V_c(\boldsymbol{r}) = V_0\delta(\boldsymbol{r})$, the expectation value is proportional to the probability density at the origin. The single-electron probability densities of the envelope functions $\Psi_{D^0}(\boldsymbol{r})$ and $\Psi_{D^-}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ at the origin of both a neutral donor and a $D^-$ ion at the center in a quantum well with a width of 5 nm can be evaluated from Fig. 9 and are summarized in Table I. The value of $V_0$ can be estimated from the observed valley-orbit splitting of a neutral donor in the bulk of $\Delta_c$=2.2 and 3.8 meV, respectively, for P and As.[18] Hence, we can evaluate the expectation values of the central-cell correction $V_c(\boldsymbol{r})$ on a neutral donor and a $D^-$ ion in a quantum well, respectively, by using the following wave functions:

$$\Phi_{D^0}(\boldsymbol{r}) = \Psi_{D^0}(\boldsymbol{r})\frac{1}{\sqrt{2}}[u_1(\boldsymbol{r}) + u_{\bar{1}}(\boldsymbol{r})]$$

TABLE I. The single-electron probability density of the envelope functions at the origin of a neutral donor $D^0$ for the (1)-valley configuration and a $D^-$ ion for the (1,1)-intravalley configuration at $\gamma$=0 and $\gamma$=3 in the bulk Si and in the Si quantum well with a width of 5 nm. The unit of the probability density is $(a_B^*)^{-3}$.

| | Bulk | | Well | |
|---|---|---|---|---|
| | $\gamma$=0 | $\gamma$=3 | $\gamma$=0 | $\gamma$=3 |
| $D^0$ | 1.2 | 2.3 | 1.7 | 2.7 |
| $D^-$ | 0.66 | 1.6 | 1.1 | 2.1 |

$$\Phi_{D^-}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \Psi_{D^-}(\boldsymbol{r}_1,\boldsymbol{r}_2) \times \frac{1}{2}[u_1(\boldsymbol{r}_1) + u_{\bar{1}}(\boldsymbol{r}_1)][u_1(\boldsymbol{r}_2) + u_{\bar{1}}(\boldsymbol{r}_2)]. \tag{7}$$

Here, $u_1(\boldsymbol{r})$ and $u_{\bar{1}}(\boldsymbol{r})$ are the Bloch functions at the bottom of the valleys (1) and $(\bar{1})$ in Fig. 1. The calculated expectation values of the central-cell correction on both the ground-state energies and the binding energy of a $D^-$ ion are summarized in Table II. It is seen that the binding energy of a $D^-$ ion becomes deeper by the central-cell correction from the value calculated in the effective-mass approximation. In the presence of the magnetic field along the [001] direction, the magnitudes of the central-cell correction for P and As are increased by constriction of the probability density of the envelope functions. For Li, on the other hand, the central-cell correction to the $D^-$ binding energy vanishes. In the bulk Si in the presence of the magnetic field or in a quantum well with an intermediate width, the symmetry is lowered incompletely and we must determine the coefficient of each valley state for a neutral donor and that of each valley configuration for a $D^-$ ion, similarly to the calculation in the stress-applied case.[18,30] This is reserved for future work.

TABLE II. The central-cell corrections on the ground-state energies of a neutral donor for the(1)-valley configuration and of a $D^-$ ion for the (1,1)-intravalley configuration and the resultant central-cell correction on the binding energy of a $D^-$ ion, $\Delta E_B(D^-)$, at $\gamma$=0 and $\gamma$=3 in the Si quantum well with a width of 5 nm. The magnitude of the central-cell correction potential $V_0$ for P and As and the binding energies calculated in the effective-mass approximation are also written.

| | P | As | Effective-mass approx. |
|---|---|---|---|
| $V_0$ | −1.83 meV$(a_B^*)^3$ | −3.17 meV$(a_B^*)^3$ | |
| $\gamma$=0 | | | |
| $D^0$ | −6.2 meV | −10.8 meV | 37.5 meV |
| $D^-$ | −7.7 meV | −13.3 meV | 4.6 meV |
| $\Delta E_B(D^-)$ | 1.5 meV | 2.5 meV | |
| $\gamma$=3 | | | |
| $D^0$ | −10.0 meV | −17.2 meV | 69.0 meV |
| $D^-$ | −15.3 meV | −26.5 meV | 19.8 meV |
| $\Delta E_B(D^-)$ | 5.3 meV | 9.3 meV | |

Finally, we mention comparison with the experimental results on the binding energy of a $D^-$ ion. The calculated values of $\epsilon_{ij}=1.82$ meV and $E_B^{D^-}=1.74$ meV of Eq. (6) agree well with the observed values[16] of 1.75 meV for Li and 1.73 meV for P in the bulk Si in the absence of the magnetic field, as mentioned in our previous paper.[24] This implies that the assumption of cancellation of the central-cell correction for the $D^-$ binding energy is appropriate for P in the bulk Si, although it does not hold for As with the binding energy of 2.05 meV. As for the magnetic-field dependence of a $D^-$ binding energy, a substitutional As and an interstitial Li were investigated in the bulk Si.[16] In the experiment, the magnetic field was applied parallel to the [111] direction up to 6 T of $\gamma=0.103$. In these weak fields, the magnetic-field-induced increase in the binding energy of a negative donor is mainly determined by the ascent of the lowest Landau level determined by the cyclotron mass $m^*$, $\frac{1}{m^{*2}}=\frac{\cos^2\theta}{m_t^2}+\frac{\sin^2\theta}{m_t m_l}$. Here, $\theta$ is the angle between the longitudinal axis of each valley and the magnetic field and $\cos\theta=1/\sqrt{3}$ irrespective of the valley index. Then, the lowest Landau level is estimated as 1.25 meV at 6 T. The observed increase in the $D^-$ binding energy at 6 T is about 1.27 and 1.2 meV for As and Li, respectively. These energies agree well with 1.25 meV of the ascent of the lowest Landau level. The little discrepancy may be attributed to the diamagnetic effect or the central-cell correction.

In summary, we investigated the spin-singlet ground state of a negative donor in the bulk Si and in $Si/SiO_2$ quantum wells in the presence of a magnetic field. We used a diffusion quantum Monte Carlo simulation with the importance sampling. By neglecting the central-cell correction, the negative donor state can be assigned by the valley indexes of two trapped electrons. In the bulk Si, the ground-state energies of negative donors of both the intervalley and the intravalley configurations split into two levels in a magnetic field along the $z$ axis and the lowest-energy state becomes the intervalley configuration of the two electrons in the valleys with their longitudinal axes perpendicular to the magnetic field. The magnetic field increases the binding energy of a negative donor and the strongest enhancement is attained for the intravalley configuration of the two electrons in the valley with the longitudinal axis parallel to the magnetic field. In the quantum well with the interface within the $x$-$y$ plane, the quantum confinement effect changes the lowest-energy state of a negative donor from the intervalley configuration in the bulk to the intravalley configuration of the two electrons in the valley with the longitudinal axis along the $z$ axis and its binding energy can be remarkably increased by the magnetic field perpendicular to the well interface.

A negative donor in $Si/SiO_2$ quantum wells has a much deeper binding energy compared to the bulk Si and it is promising for realizing a spin-dependent electron charge-transfer event $D^0D^0 \rightarrow D^+D^-$ in donor-spin readout proposed by Kane.[23]

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