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Negative donors in multivalley semiconductors: Diffusion quantum Monte Carlo simulations

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Ground states of the D$^-$ ion in multivalley semiconductors have been investigated using a diffusion quantum Monte Carlo method, under the condition that the central-cell correction for a donor ion can be neglected. The D$^-$ binding energy $E_B^{\mathrm{D}^-}$ can be simply approximated for the intravalley configuration with the use of a donor binding energy $E_B^{\mathrm{D}^0}$, as $E_B^{\mathrm{D}^-} \simeq 0.055 E_B^{\mathrm{D}^0}$, if the anisotropy of the effective mass is not so large. The anisotropy of the effective mass being large, the D$^-$ binding energy increases greater than $0.055 E_B^{\mathrm{D}^0}$. This is due to the enhancement of the correlation effect between two electrons in a D$^-$ ion with lowering dimension. For the intervalley configuration, the D$^-$ binding energy is further increased because the repulsive Coulomb energy between trapped electrons can be effectively suppressed. Our calculated results reproduce well the experimental ones for Si and Ge, in which the intravalley or the intervalley configuration is well controlled.

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I. INTRODUCTION

As the solid state candidates for qubits in quantum information processing, semiconductor-based systems have been extensively examined. Following the proposal by Kane,[1] there has been a great deal of activity to develop a silicon-based quantum computer architecture such as direct exchange interaction[2] between electron spins in a donor and charge qubits[3] composed of two donors. Considering the multivalley structure of the Si conduction band, the intervalley interference has important consequences for single-qubit operation.

Column IV elemental semiconductors such as silicon, germanium, and diamond are multivalley semiconductors, and the minima of the conduction band are located at several equivalent points in the Brillouin zone. The effective mass parallel or perpendicular to the rotational axis in each valley becomes different, that is, an anisotropic effective mass, contrary to the case of GaAs with an isotropic effective mass, in which the conduction band minimum is located at the Γ point in the Brillouin zone. It is well known that a neutral state of a donor (D^0) is affected by the anisotropy of the effective mass. A neutral donor can weakly bind an additional electron. The resultant negative donor is referred to as a D$^-$ ion. Repulsive Coulomb energy between two trapped electrons, i.e., the energy difference between a D$^-$ ion and two neutral donors, is called U in the Hubbard model. This U determines a magnitude of an antiferromagnetic exchange interaction between two separated, localized electrons with a transfer integral t as $4|t|^2/U$. This antiferromagnetic exchange interaction prevails over the direct ferromagnetic exchange interaction at a large interval.[4]

With respect to the D$^-$ state, a lot of theoretical studies have been performed by various methods, such as the variational method,[5–7] diffusion quantum Monte Carlo method,[8] and full configuration-interaction approach.[9] However, they have been limited to the single valley case. For multivalley semiconductors, a simple variational calculation has been performed on the D$^-$ ion states by Natori and Kamimura:[10] In the calculated binding energies for a D$^-$ ion, ϵ_{ii} in the intravalley electron configuration and ϵ_{ij} in the intervalley one are rather qualitative but not quantitative sufficiently, since both the correlation term in the variational wave function and the valley-orbit splitting are neglected.

Extensive experimental studies have been performed by Narita's group for an isolated D$^-$ ion in Si and Ge. They have pointed out that extremely low impurity concentration and compensation are indispensable: The concentration dependence of the D$^-$ state spectra indicates the transition from a shallow isolated D$^-$ state to a deeper bound one in which electrons are trapped by two or more neutral donors.[11] The electron binding energies of an isolated D$^-$ ion state in Ge are determined to be 0.625 and 0.75 meV for Sb and As impurities, respectively, using the long-wavelength photoconductivity thresholds[12] at low temperatures. Uniaxial stress effect on the electron binding energy of an isolated D$^-$ state has also been investigated; D$^-$ binding energies are shifted to 0.55 meV (Sb) and 0.57 meV (As) with the high [111] uniaxial stress where the single valley configuration is realized. For Si, on the other hand, the D$^-$ binding energies are similarly determined to be 1.73, 2.05, and 1.75 meV for P, As, and Li impurities, respectively, in the stress free case.[13] Norton obtained a similar value of 1.7 meV for both P and As impurities from the photoconductivity spectra[14] at a low temperature. When the [100] uniaxial stress is applied,[13] the D$^-$ binding energy decreases initially and then increases with increasing stress for P and As impurities. However, the high stress limit was not attained in their experiments. The D$^-$ binding energy for an interstitial Li impurity decreases linearly as the [100] stress increases and converges at a limit of high stress with a constant value of 1.55 meV.

Such stress dependences of the binding energies of D$^-$ ions for P and As substitutional impurities in Si were first investigated by Larsen[15] and then refined by Oliveira and Falicov[16] in consideration of the valley-orbit interaction.[17–19] They obtained the zero-stress binding energies of the D$^-$ state in P-doped Si as 1.04 (Ref. 15) and 2.23 meV.[16] For the interstitial Li impurity, on the other hand, Larsen has pointed out[15] that the inverted structure of the valley-orbit split ground-state levels of Li donors[19] gives quite different stress

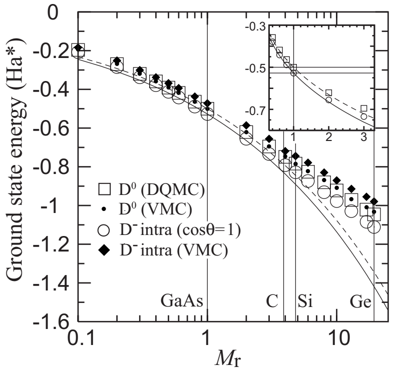

FIG. 1. Ground-state energies of a neutral donor D^0 and a D^- ion for the intravalley configuration as a function of the effective mass ratio M_r, calculated by the DQMC method, the VMC method, and the geometric averaged effective mass [Eq. (4)] (a broken line for D^0 and a solid line for D^-). An inset shows them in a linear scale around $M_r=1$. The two horizontal lines indicate the values of -0.5 and -0.5275 Ha*.

dependence of the D^- binding energy, i.e., a pure intervalley energy ϵ_{ij} at zero stress and a pure intravalley energy ϵ_{ii} at the high stress limit. In these studies, on the stress dependence of the D^- ion state, however, the effect of the anisotropic effective mass in each valley was neglected.

Our purpose is to accurately calculate the binding energy of the D^- ground state for multivalley semiconductors and to quantitatively clarify both effects of the anisotropy of the effective mass and the multivalley structure. The binding energy of a D^- ion is very small and hence the correlation effect between the two trapped electrons is essentially important. In order to treat the correlation effect appropriately, we used the diffusion quantum Monte Carlo (DQMC) method.[20]

II. CALCULATION METHOD

If the central-cell correction is neglected in multivalley semiconductors, each electron of the D^- ion belongs to a specific valley among several equivalent valleys. Therefore, an electron configuration of a D^- ion is assigned by the valley configuration: the *intravalley* (*intervalley*) configuration if two trapped electrons belong to the same (different) valley, respectively. In the effective mass approximation, the Hamiltonian for a D^- ion with the intravalley configuration is given by

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

$$H_1(\boldsymbol{r}_n) = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2}\right) - \frac{1}{2M_r}\left(\frac{\partial^2}{\partial z_n^2}\right) - \frac{1}{r_n}. \qquad (1)$$

Here, r_{12} is the distance between two electrons and $H_1(\boldsymbol{r}_n)$ is the single electron Hamiltonian for a neutral donor D^0. M_r is the ratio of the longitudinal effective mass m_l^* to the transverse effective mass m_t^*, i.e., $M_r = m_l^*/m_t^*$. For example, $M_r = 1.0$, 3.89, 4.81, and 19.5 for GaAs, diamond, Si, and Ge, respectively.[21] In Eq. (1), the energy and the length are measured in the effective atomic units of Ha$^* = m_t^* e^4/(8\epsilon h^2)$ and $a_B^* = \epsilon h^2/(\pi m_t^* e^2)$, respectively. In the case of the intervalley configuration, the longitudinal axis z in the single electron Hamiltonian becomes different for each electron. The binding energy of a D^- ion is calculated as

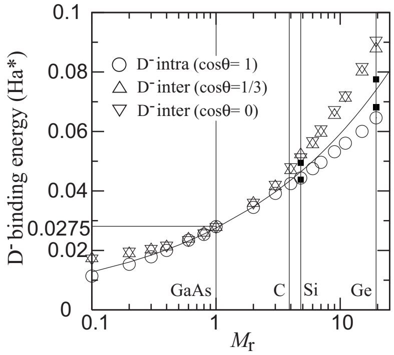

FIG. 2. Binding energies of D^- ions for both the intravalley and the intervalley configurations as a function of the effective mass ratio M_r. Experimental values for Li-doped Si (Ref. 13) and Sb-doped Ge (Ref. 12) in the stress free and in the high stress limit are shown by solid squares. Here, θ is the angle between two longitudinal axes of each valley. The results for the geometrically averaged effective mass [Eq. (5)] is also plotted by a solid line.

$$E_B^{D^-} = E_{D^0} - E_{D^-}, \qquad (2)$$

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

We used the DQMC method with an importance sampling[20] to calculate the ground-state energies, E_{D^0} and E_{D^-}. In the DQMC method, a diffusion constant in each direction is inversely proportional to the corresponding effective mass of each electron. Hence, we can easily implement both the anisotropy of the effective mass and the multivalley structure by using the DQMC method. We assumed the spin-singlet ground state for a D^- ion and adopted the following simple trial functions for D^0 and D^- states in the importance sampling for the intravalley case,

$$\psi_{D^0}^{\text{trial}} = \exp\left(-\sqrt{\frac{x^2+y^2}{a_1^2} + \frac{z^2}{b_1^2}}\right),$$

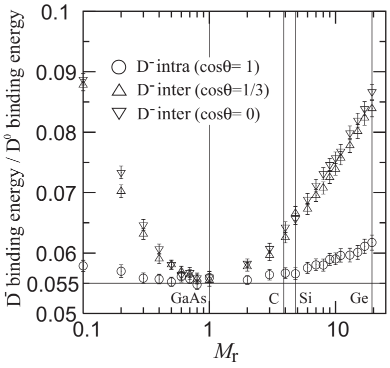

FIG. 3. Ratio of a D^- binding energy to a neutral donor binding energy as a function of the anisotropy of the effective mass, M_r.

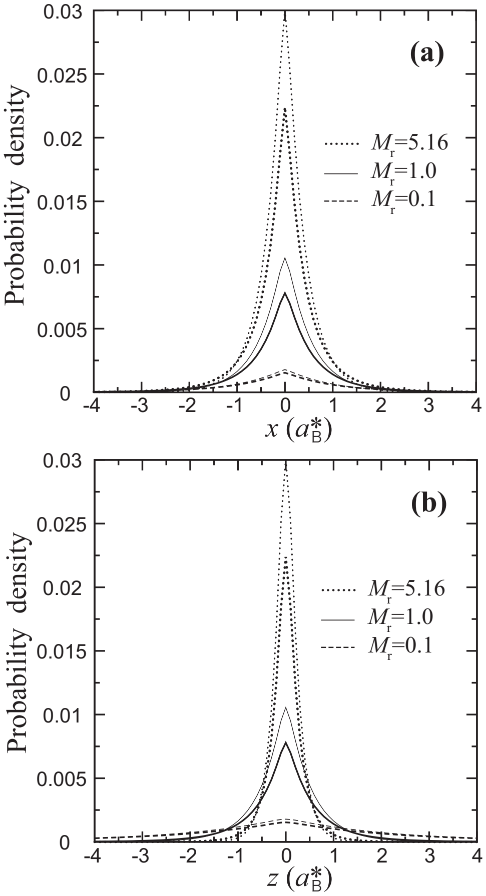

FIG. 4. Probability density distributions of both a neutral donor (thin lines) and a D^- ion (thick lines) for the intravalley configuration, along the (a) transverse direction and the (b) longitudinal direction.

$$\psi_{D^-}^{\text{trial}} = \exp\left(-\sqrt{\frac{x_1^2+y_1^2}{a_2^2}+\frac{z_1^2}{b_2^2}}-\sqrt{\frac{x_2^2+y_2^2}{a_2^2}+\frac{z_2^2}{b_2^2}}\right), \quad (3)$$

where a_i and b_i are the variational parameters related to the transverse and the longitudinal extensions of the wave function around a donor. The parameters are optimized with a variational Monte Carlo (VMC) simulation.

III. NUMERICAL RESULTS

In Fig. 1, the ground-state energies for the intravalley configurations of a neutral donor and a negative donor ion with the DQMC method are plotted as a function of the anisotropy of the effective mass, M_r. Here, θ is the angle between the longitudinal rotational axes of the valleys. For example, θ=0 in the intravalley case, θ=90° in the intervalley cases of Si and diamond, and cos θ=1/3 in the intervalley case of Ge. It should be mentioned that the two-different-valley configuration with θ=180° for Si is equivalent to the intravalley one. With the isotropic effective mass of M_r=1.0, the ground-state energies of neutral donor and negative donor states are well known to be −0.5 and −0.5275 Ha*,[8] respectively. Our DQMC calculations reproduce well these values at M_r=1.0, contrary to our previous simple variational calculation.[10] If we use the geometric average of the anisotropic effective mass instead of the anisotropic effective mass itself, the ground-state energies can be approximated as

$$E_{D^0} \simeq -0.5M_r^{1/3},$$

$$E_{D^-} \simeq -0.5275M_r^{1/3}. \quad (4)$$

It is seen in Fig. 1 that these approximations underestimate the ground-state energies except for M_r=1.0. The numerical results of the VMC simulations are also presented in Fig. 1. The agreement between the DQMC and VMC results is very good for a neutral donor state, but the VMC calculation cannot give a bound D^- state owing to the poor assumption for the variational wave function for a D^- ion [Eq. (3)]. On the other hand, the DQMC method gives a shallow-bound state for D^-. The resulting binding energy ϵ_{ii} is plotted in Fig. 2 with ϵ_{ij} for the intervalley configuration. The binding energy of the D^- ion increases monotonically as a function of M_r as seen in Fig. 2, since the contribution of the longitudinal kinetic energy is suppressed. In the intervalley configuration, the D^- binding energy increases with increasing θ, which is

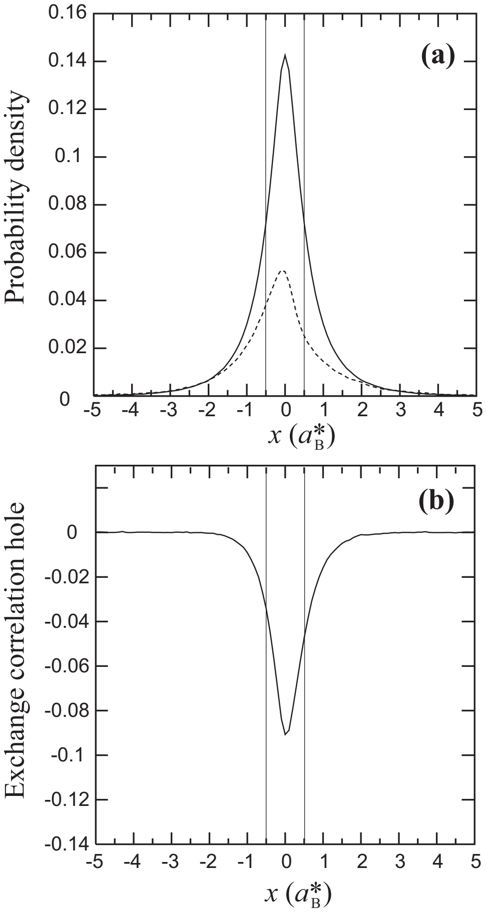

FIG. 5. (a) Correlated probability density distributions (broken line) of a D^- ion for the intravalley configuration, when the other electron is located at $\boldsymbol{r}$=(0.5,0,0), and (b) exchange-correlation hole distribution, along the transverse x axis. In (a), the probability density distribution for a D^- ion is also drawn by a solid line. Here, M_r=19.5 is assumed, corresponding to Ge.

TABLE I. Calculated values of D^- binding energies (meV) using the DQMC method and Eq. (6) and observed ones in the stress free and in the high stress limit (Li-, P-, and As-doped Si and Sb- and As-doped Ge). The neutral donor binding energy $E_B^{D^0}$ (meV) calculated using the DQMC method is also shown. The longitudinal effective mass m_l^*, the transverse effective mass m_t^* in a unit of m_0, and the relative permittivity for Si and Ge are also shown (Ref. 21).

	$m_t^*(m_0)$	$m_l^*(m_0)$	ϵ_r	$E_B^{D^0}$	$E_B^{D^-}$	$E_B^{D^-}$ (Expt.)			
Si	0.1905	0.9163	12.1	27.7	$\epsilon_{ii}=1.57$	High stress:	1.55(Li)[a]		
					$\epsilon_{ij}=1.82$	Stress free:	1.75(Li)[a]		
					1.74 [Eq. (6)]	Stress free:		1.73, 1.7(P)[a,c]	2.05, 1.7(As)[a,c]
Ge	0.0807	1.57	16.5	8.43	$\epsilon_{ii}=0.52$	High stress:	0.55(Sb)[b]		0.57(As)[b]
					$\epsilon_{ij}=0.71$				
					0.66 [Eq. (6)]	Stress free:	0.625(Sb)[b]		0.75(As)[b]

[a] Reference 13.

[b] Reference 12.

[c] Reference 14.

attributed to the reduction of the electron-electron Coulomb interaction. The geometric average mass approximation of Eq. (4) gives the following relation in the intravalley case,

$$\epsilon_{ii} \simeq 0.0275 M_r^{1/3}; \tag{5}$$

however, it is clearly seen that Eq. (5) slightly overestimates the intravalley D^- binding energies.

To investigate the relation between the binding energies of a neutral donor and a D^- ion, we show their ratio as a function of M_r in Fig. 3. The remarkable result is that the ratio is roughly constant in the intravalley case and it takes values of 0.055–0.06 for $0.1 < M_r < 10.0$, as is the case with an isotropic effective mass[22] (0.055). This scaling relationship enables us to evaluate the D^- binding energy simply as $\epsilon_{ii} \simeq 0.055 E_B^{D^0}$ for the intravalley case. The geometric average mass approximation overestimates both binding energies of ϵ_{ii} and $E_{\mathrm{B}}^{D^0}$, and hence their ratio has a nearly constant value in a somewhat wide range of $0.1 < M_r < 10.0$. This approximation becomes poor outside this range, being caused by the enhancement of the electron correlation effect, which is characteristic in lower dimensional systems. It should be mentioned that $E_B^{D^0}$ can be estimated easily by the simple variational calculations. In the intervalley case, on the other hand, this simple scaling relation does not hold and the ratio is increased with increasing mass anisotropy because of the reduction of the Coulomb interaction energy between two trapped electrons.

Next, we show the distribution of the probability density of an electron for both D^0 and D^- states in Fig. 4. It is seen that an electron of a D^- state is distributed more widely than that of a D^0. This results from the repulsive Coulomb interaction between two electrons in a D^- ion. Furthermore, the anisotropic distribution can be recognized for $M_r \neq 1.0$. Finally, in Fig. 5, we present both the correlated probability density and the exchange-correlation hole distributions along the transverse x axis, in which the position of another electron in a D^- ion is fixed at $\boldsymbol{r}=(0.5,0,0)$ for the intravalley case of Ge. The calculated exchange-correlation hole has the maximum amplitude at the position of a donor ($x=0$) and has a larger amplitude at the position of the other electron because of the correlation effect; as a result, the exchange-correlation hole is asymmetric. Such an asymmetric fashion is also confirmed for the Ne atom.[23]

IV. DISCUSSION AND CONCLUSION

Numerical results on the D^- binding energies for Si and Ge are summarized in Table I with the experimental results. First, we compare calculated D^- binding energies with the observed ones for Li-doped Si, 1.75 meV (stress free) and 1.55 meV (high stress limit).[13] Larsen has pointed out[15] that they correspond to the intervalley binding energy ϵ_{ij} and the intravalley one ϵ_{ii}, respectively. Our calculations give values of 1.82 meV (ϵ_{ij}) and 1.57 meV (ϵ_{ii}), which agree well with the observed values (solid squares in Fig. 2). Next, we compare our results with Sb- and As-doped Ge, where the D^- binding energies observed at the high stress limit are 0.55 and 0.57 meV, respectively,[12] with the negligible chemical shift. The calculated value for the intravalley configuration (0.52 meV), which corresponds to the high stress case, agrees well with the experimental one (see Fig. 2). In our previous calculations of the D^- binding energies,[10] $\epsilon_{ii}=0.74$ meV and $\epsilon_{ij}=1.01$ meV for Si and $\epsilon_{ii}=0.22$ meV and $\epsilon_{ij}=0.48$ meV for Ge were obtained. Larsen improved the calculation and obtained[24] the values of $\epsilon_{ii}=1.50$ meV and $\epsilon_{ij}=1.66$ meV for Si. All these values are smaller than those in Table I obtained by present DQMC calculations. In the DQMC method, the correlation effect between two electrons in a D^- ion can be considered accurately and hence the ground-state energy of a D^- ion is lowered, giving a larger binding energy in comparison with previous results.

In general, the effect of the central-cell correction for a donor ion and the associated valley-orbit splitting[17,18] must be considered. Larsen[15] and Oliveira and Falicov[16] succeeded in explaining qualitatively the stress dependence of the D^- binding energy for P- and As-doped Si by taking into account of the valley-orbit splitting, but quantitative agreement with the experimental results was not so good. Here, we try to estimate the D$^-$ binding energy in the stress free case with the simple assumption. The short-range interaction elicits the central-cell correction, in which the states assigned to each valley are mixed.[10] The ground state of a neutral donor can be written as a linear combination of each valley state with an equal weight. Hence, the ground state of a D$^-$ ion can be obtained as the linear combination of the intravalley and intervalley configurations. If the central–cell corrections for the D$^-$ and the D^0 ground states are assumed to be the same, the D$^-$ binding energy can be simply approximated as

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

Here, g is related to the valley degeneracy and takes the values of 3 and 4 for Si and Ge, respectively.[25] The same relation as Eq. (6) has also been shown by Larsen,[24] and the D$^-$ binding energy was approximated as 1.61 meV for P-doped Si at zero stress.

Now, we try to compare our numerical results based on Eq. (6) with the experimental ones in the stress free case. As for Si, the binding energy is estimated as 1.74 meV from Eq. (6) with ϵ_{ii} (1.57 meV) and ϵ_{ij} (1.82 meV) in Table I, which agrees well with the observed values for P- and As-doped Si (1.7 meV) (Ref. 14) and for P-doped Si (1.73 meV).[13] As for Ge, on the other hand, Taniguchi and Narita observed D$^-$ binding energies of 0.625 and 0.75 meV in the stress free case for Sb- and As-doped Ge, respectively.[12] A remarkable chemical shift is observed in the stress free case. Equation (6) gives the D$^-$ binding energy of 0.66 meV in satisfactory agreement with 0.625 meV for Sb-doped Ge. However, this simple approximation cannot explain the observed D$^-$ binding energies for As-doped Si (2.05 meV) (Ref. 13) and As-doped Ge (0.75 meV).[12] As impurities have the largest valley-orbit splitting[17,18] among donor impurities in Si and Ge. For such a case, the effect of the valley-orbit splitting must be considered for the D$^-$ ground-state calculation.

In conclusion, we studied the D$^-$ ion ground state in the multivalley semiconductors using the DQMC method when the central-cell correction of a donor ion can be neglected. The D$^-$ binding energy ϵ_{ii} for the intravalley configuration can be well approximated as $\epsilon_{ii} \simeq 0.055 E_B^{\mathrm{D}^0}$ with an accuracy of less than 10% in the range of the effective mass ratio of $0.1 < M_r < 10.0$. With increasing anisotropy of the effective mass, the ratio is increased larger than 0.055, since the correlation effect between two electrons in a D$^-$ ion is enhanced in lowering dimensions. In the intervalley case, the D$^-$ binding energy ϵ_{ij} is increased as the angle between the longitudinal axes of each valley increases. Calculated results reproduce well the observed D$^-$ binding energies for Si and Ge under the experimental situation where the intravalley or the intervalley configuration is realized.

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[1] B. E. Kane, Nature (London) **393**, 133 (1998).
[2] B. Koiller, X. Hu, and S. DasSarma, Phys. Rev. Lett. **88**, 027903 (2001).
[3] X. Hu, B. Koiller, and S. DasSarma, Phys. Rev. B **71**, 235332 (2005).
[4] H. Masu, T. Yamada, J. Nakamura, and A. Natori, Phys. Rev. B **74**, 075312 (2006).
[5] C. L. Perkeris, Phys. Rev. **112**, 1649 (1958).
[6] C. L. Perkeris, Phys. Rev. **126**, 1470 (1962).
[7] J. L. Zhu, J. H. Zhao, and J. J. Xiong, Phys. Rev. B **50**, 1832 (1994).
[8] T. Pang and S. G. Louie, Phys. Rev. Lett. **65**, 1635 (1990).
[9] O. A. Al-Hujaj and P. Schmelcher, Phys. Rev. A **61**, 063413 (2000).
[10] A. Natori and H. Kamimura, J. Phys. Soc. Jpn. **43**, 1270 (1977).
[11] M. Taniguchi and S. Narita, Solid State Commun. **20**, 131 (1976).
[12] M. Taniguchi and S. Narita, J. Phys. Soc. Jpn. **43**, 1262 (1977).
[13] S. Narita, T. Shinbashi, and M. Kobayashi, J. Phys. Soc. Jpn. **51**, 2186 (1982).
[14] P. Norton, Phys. Rev. Lett. **37**, 164 (1976).
[15] D. M. Larsen, Phys. Rev. B **23**, 5521 (1981).
[16] L. E. Oliveira and L. M. Falicov, Phys. Rev. B **33**, 6990 (1986).
[17] J. H. Reuszer and P. Fisher, Phys. Rev. **135**, A1125 (1964).
[18] R. L. Aggarwal and A. K. Ramdas, Phys. Rev. **140**, A1246 (1965).
[19] R. L. Aggarwal, P. Fisher, V. Mourzine, and A. K. Ramdas, Phys. Rev. **138**, A882 (1965).
[20] B. L. Hammond, J. W. A. Lester, and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
[21] *Semiconductors—Basic Data*, edited by O. Madelung (Springer, Berlin, 1996).
[22] M. A. Lampert, Phys. Rev. Lett. **1**, 450 (1958).
[23] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[24] D. M. Larsen, in *Physics in High Magnetic Fields*, edited by S. Chikazumi and N. Miura (Springer, Berlin, 1981), p. 120.
[25] Two valleys with the same longitudinal axis in Si are equivalent with each other and the effective valley degeneracy of Si becomes 3 instead of 6.