# Antiferromagnetic exchange interactions among dopant electrons in Si nanowires

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Magnetic interactions among substitutional dopant impurities in silicon nanowires are investigated theoretically using density functional calculations. Our results show that while dopant impurities in silicon nanowires have no magnetic ordering in the ground state, a magnetic moment imposed at an impurity by applying an effective local magnetic field induces a magnetic moment, smaller in magnitude and opposite in sign, at an adjacent impurity, demonstrating an antiferromagnetic coupling between the impurity spins. The sign of the calculated Heisenberg exchange parameter *J* between the impurity spins also corresponds to the antiferromagnetic coupling and its magnitude decreases monotonically as the distance between impurities increases. Our results suggest that, while there is no static magnetic moment on dopant impurity atoms, a direct exchange interaction between the impurity spins, confirming the suggestion from a recent experimental work observing the Kondo-like temperature dependence of the electrical resistance of doped silicon nanowires.

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#### I. INTRODUCTION

Low-dimensional materials such as semiconductor nanocrystals and nanowires are characterized by the quantum confinement and large surface-to-volume ratio which result in increased energy gaps and strong surface effects on electronic structures. These intrinsic low-dimensional properties in semiconductors give rise to phenomena quite different from the bulk materials, as exemplified by general difficulty in carrier doping due to the high carrier activation energy resulting from the reduced screening [1,2], the carrier compensation by surface/interface charge traps [1,3], and the formation of deactivating donor-pair defects [4,5], etc. Silicon nanowires (Si NWs) are especially of great interest as they have been considered as one of the most practical and reliable building blocks for future device applications, largely owing to its compatibility with the conventional silicon technology that has matured over decades. Many of possible applications have already been demonstrated experimentally, such as field-effect transistors [6–11], chemical and biological sensors [12], solar cells [13-15], and switches [16], to name a few. While one basically makes use of only the electronic charge degrees of freedom for the above-mentioned applications, Si NWs are also well suited for spintronic applications as channel materials owing to the weak spin-orbit interaction, resulting in a long spin relaxation time and a large spin diffusion length, as demonstrated recently [17–19].

Magnetism has been of interest mainly in materials consisting of elements from d or f blocks in the Periodic Table, where strong intra-atomic Coulomb interactions play an important which originates purely from atomic s or p orbitals is relatively rare, with occasional examples mainly from carbon-based nanostructures [20-22]. As for silicon, some signatures of magnetic interactions in the phosphorus-doped bulk silicon were reported from the magnetoresistance and the electron spin resonance measurements [23–29]. Spin coupling among phosphorus atoms in bulk silicon is also of great interest as a material platform for the qubit entanglement towards the quantum computing [30,31]. Recently, a local antiferromagnetic coupling between spins localized around phosphorus impurities was suggested in heavily phosphorous-doped Si NWs from a transport experiment [32], where the magnetic susceptibility of Si NWs deduced from the magnetoresistance measurements showed an antiferromagnetic nature. While the majority of research on the magnetism in semiconductors in their bulk or low-dimensional forms have been focused on achieving a long-range magnetic ordering via the magnetic impurity doping [33-35], this experimental study implies an impact on the charge and spin transport properties in general semiconductor nanowires without the long-range magnetic order. Moreover, it is a very interesting result in the sense that it suggests a magnetic interaction relevant in Si, a representative conventional semiconductor, without incorporation of any transition metal impurity. However, direct evidence of the spin coupling and understanding of underlying mechanisms have been lacking.

role. Meanwhile, intrinsic magnetism in semiconductors

In this paper, we report our theoretical results on magnetic interactions between substitutional phosphorus or boron impurities in a Si NW, based on the first-principles calculations. We obtain nonmagnetic ground states for phosphorus-doped Si NWs, consistent with experimental observation that there is no static long-range magnetic order in Si NWs. However, when we use the constrained density functional theory (DFT) scheme

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FIG. 1. (Color online) Atomic structure of the [110] Si NW of diameter 8.4 Å seen (a) along the axis direction and (b) from the side. Smaller gray (brighter) and larger magenta (darker) balls represent hydrogen and silicon atoms, respectively.

to force a spin moment around an impurity atom, we find that a spin moment with opposite sign is induced at another impurity atom nearby, which reveals an antiferromagnetic coupling between impurity atoms. We also explicitly confirm the antiferromagnetic spin coupling by calculating the Heisenberg exchange parameter J as a function of the impurity-impurity distance, and find that this spin coupling can be understood by the direct exchange interaction between the singly occupied donor or acceptor states which are hydrogenic within the effective mass approximation.

#### **II. CALCULATION METHOD**

Our first-principles calculations are based on DFT with the local spin density approximation [36] and the *ab initio* norm-conserving pseudopotentials [37] in the fully separable form [38] as implemented in the SIESTA code [39]. Electronic wave functions are expanded with localized pseudoatomic orbitals (PAOs, the double  $\zeta$  polarization basis set), with the cutoff energy of 500 Ry for the real-space mesh. We consider a Si NW in [110] and employ a supercell which contains 18 primitive unit cells (69.24 Å long) of the Si NW along the axis, separating the wire and its periodic images by a vacuum region of over 10 Å to avoid spurious interaction among them. Because our supercell includes a large enough number of primitive unit cells along the wire axis, only the  $\Gamma$  point is sampled for the Brillouin-zone integration. Atomic positions for the perfect Si NW are fully relaxed until the residual force on each atom is smaller than 0.02 eV/Å. For Si NWs doped with substitutional phosphorus or boron atoms, we simply replace silicon atoms in the optimized perfect Si NW by phosphorus or boron atoms without any further relaxation [40].

# **III. CONSTRAINED DFT SCHEME**

The atomic structure of the [110] Si NW which we adopt in this study is shown in Fig. 1. The diameter of the wire is about 8.4 Å, and one or two hydrogen atoms are bonded to each silicon atom on the NW surface to passivate the dangling bonds, depending on the number of neighboring silicon atoms of the surface silicon atoms. The supercell used in this work, including 18 primitive unit cells along the axis as mentioned above, contains 288 silicon and 216 hydrogen atoms. Since phosphorus impurities prefer substitutional sites near the center of the Si NW in general [5], we replace one of two equivalent central silicon atoms by a phosphorus atom.

The single phosphorus atom in our Si NW produces a shallow donor level as in bulk silicon, occupied by an electron. Within the standard DFT scheme with the local spin density approximation, we obtain a nonmagnetic ground state with spin-up and spin-down donor states being equally occupied by half an electron each, in accordance with previous calculations [41]. This nonmagnetic ground state implies that the spin direction of the electron at the impurity state changes in time without any preferred direction. To impose a finite spin moment on the phosphorus atom, i.e., to obtain a converged electron density distribution with a net spin moment, we need to set up a constraint to the DFT total-energy functional as follows:

$$E_{\text{CDFT}}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \lambda_{a}, m_{a}] = E_{\text{DFT}}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] + \sum_{a} \lambda_{a} \left[ \int f(\mathbf{r} - \mathbf{r}_{a})[n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})]d^{3}\mathbf{r} - m_{a} \right], \quad (1)$$

where  $E_{\text{DFT}}$  represents the total-energy functional of original DFT which depends on the electron density  $n_{\sigma}(\mathbf{r})$  for each spin ( $\sigma = \uparrow$  or  $\downarrow$ ), and the quantity in the large bracket is a penalty function to force the integrated spin density around the phosphorus atom at  $\mathbf{r}_a$  to the finite magnetic moment  $m_a$ , with the Lagrange multiplier  $\lambda_a$  attached. Here  $f(\mathbf{r})$  is a function decaying with the distance r, for which we use a Gaussian function. By minimizing  $E_{\text{CDFT}}$  with respect to  $n_{\sigma}(\mathbf{r})$ and  $\lambda_a$  for given  $m_a$ , we obtain the electron density which gives the magnetic moments  $m_a$ . In this case, the functional derivative of  $E_{\text{CDFT}}$  with respect to  $n_{\sigma}(\mathbf{r})$  gives the original DFT one-electron Hamiltonian  $H_{\sigma,\text{DFT}} = \delta E_{\text{DFT}} / \delta n_{\sigma}(\mathbf{r})$  plus a new effective potential,  $\pm \lambda_a f(\mathbf{r} - \mathbf{r}_a)$ , where plus and minus signs are for  $\sigma = \uparrow$  and  $\downarrow$ , respectively. Thus minimizing  $E_{\text{CDFT}}$  instead of  $E_{\text{DFT}}$  corresponds to applying effective magnetic fields around the phosphorus atoms to impose magnetic moments.

# IV. DEMONSTRATION OF ANTIFERROMAGNETIC EXCHANGE INTERACTION

Using the constrained DFT scheme as just described, we investigate how a local spin around a phosphorus atom polarizes electron clouds nearby. First we consider a situation in which there are two substitutional phosphorus atoms separated by a distance and a spin moment is forced around only one of the two phosphorus atoms by applying a local effective magnetic field. The real-space spin density,  $n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})$ , of this configuration is shown in Fig. 2(a), where one can see a spin-polarized electron cloud, which is overall in the spin-up state, around the left phosphorus atom. The applied effective magnetic field is confined by a Gaussian function  $f(\mathbf{r}) = \exp[-(\mathbf{r}/\mathbf{r}_s)^2]$  with an effective radius  $\mathbf{r}_s$ , so the spin density far outside this radius from the left phosphorus atom is the self-consistent response of the electron to the spin moment of the left phosphorus atom. Here we set  $r_s$  to 4 Å, about the Si NW radius used in this study. Obtained self-consistent electron density shows that there is a significant spin distribution around the right phosphorus atom which is six primitive unit cells



FIG. 2. (Color online) Real-space spin density distribution in Si NW containing (a) two and (b) three substitutional phosphorus atoms, where the effective magnetic field is applied around the leftmost phosphorus atom. Spin density is shown on a plane containing the wire axis, and the atomic structure is displayed only by sticks for clarity. Yellow sticks represent the position of phosphorus atoms. Note that the color scales are different between (a) and (b), so that the same colors represent different spin density values.

(23 Å) apart from the left one. The integrated spin moment of the spin distribution around the right phosphorus atom, which is the integral term inside the large bracket in Eq. (1), is in the opposite direction and its magnitude is about 30% of that of the left phosphorus atom. This result shows clearly that a spin moment at a phosphorus atom induces an opposite spin moment at another phosphorus atom nearby, implying the antiferromagnetic exchange interaction between spins at different phosphorus atoms.

We found another indication of the antiferromagnetic nature of the exchange interaction between phosphorus dopants using similar constrained DFT calculations with a different atomic configuration involving three phosphorus atoms along the wire axis. We applied a local effective magnetic field on the leftmost phosphorus atom only and analyzed spin moments of the three phosphorus atoms. Our result is shown in Fig. 2(b), where the most intense spin density is visible at the leftmost phosphorus atom. The second phosphorus atom is placed three primitive unit cells (11.5 Å) to the right from the first one. Much less distinct spin density distribution is present around the second phosphorus atom as a response to the spin moment of the first phosphorus atom, with an integrated spin moment which is much smaller in magnitude but again opposite in sign compared with that of the first phosphorus atom. The third phosphorus atom, which is located three primitive unit cells (11.5 Å) right from the second one, has the opposite spin moment direction to that around the second phosphorus atom in turn, hence the same spin direction with the first phosphorus atom. Interestingly, the third phosphorus atom has a larger spin moment magnitude than the second one even though the third phosphorus atom is farther from the first one than the second one and the supercell is long enough (69.24 Å long) to isolate the three phosphorus atoms in the nanowire. This might seem contradictory to a natural expectation that the induced spin moment in response to the forced spin



FIG. 3. (Color online) Exchange parameter J [multiplied by  $(0.5\mu_B)^2$ ] as a function of the distance between two phosphorus atoms and between two boron atoms. The impurity-impurity distance is in the number of primitive unit cells, with the background atomic structure drawn in the scale that matches the *x*-axis unit.

moment should decrease as the distance increases between them. In fact, this expectation of the distance dependence holds true when only two phosphorus atoms are present, which we will discuss below with Fig. 3. Meanwhile, when we try to describe the situation of the three phosphorus atoms within a simple  $3 \times 3$  tight-binding Hamiltonian consisting of identical nearest-neighbor hopping energies and on-site energies with one orbital basis on each atom, an eigenstate of the Hamiltonian is consistent with the spin density in Fig. 2(b), i.e., the eigenstate has finite orbital weights on the first and third atoms while no weight at the middle atom.

In the above calculations with the two or three dopants, the spin density is distributed over several Si atoms around each phosphorus atom while there is no noticeable spin density in the middle of two neighboring dopant atoms. It is likely that the magnetic interaction in this system can be well described by a direct exchange interaction between the effective hydrogenic orbitals of shallow donor states in a semiconductor [31,42]. The nature of the exchange interaction can be revealed explicitly by calculating the exchange parameter J which appears in the Heisenberg model  $H = J \sum_{(i,j)} \mathbf{S}_i \cdot \mathbf{S}_j$ , where  $\langle i, j \rangle$  represents the summation over nearest-neighbor sites. We obtain the parameter J from the DFT total-energy difference between parallel and antiparallel spin configurations of two phosphorus atoms, stabilizing each spin configuration by the constrained DFT scheme described by Eq. (1), with a same spin moment m for two phosphorus atoms for the parallel configuration and  $\pm m$  for the antiparallel one. Here we choose  $m = 0.5 \mu_B$ . The result as a function of the phosphorus-tophosphorus (P-P) distance is displayed in Fig. 3. The obtained parameter J decreases monotonically with the increasing P-P distance. It is positive over all distances, indicating clearly the antiferromagnetic nature of the exchange interaction. With the increasing P-P distance, the J seems to approach monotonically to zero. This behavior also supports the direct exchange nature between the two donor orbitals, as mentioned above, at the same time excluding other possible types of exchange interactions such as RKKY for which J would oscillate between different signs as a function of the P-P distance [43]. Our model with the direct exchange interaction between the effective hydrogenic orbitals of shallow donor states is also supported by the experimental evidence observed in heavily phosphorus-doped Si NWs ( $n_d > 3 \times 10^{18} \text{ cm}^{-3}$ ), where the dopant concentration ( $n_d$ ) is large enough for impurity states to directly overlap and form a metallic band [32].

Having acknowledged the possibility of direct exchange interactions between donor states, we also consider a similar case with acceptors. We have conducted constrained DFT calculations with boron impurities. As displayed in Fig. 3, the result shows a similar behavior with the phosphorus case although the overall magnitude of J is reduced. This result is also consistent with the direct exchange interaction between acceptor states. The smaller value of J can be understood by the fact that the effective Bohr radius of the acceptor level is smaller than that of the donor level in general due to larger effective masses of valence bands than those of conduction bands in semiconductors.

# V. ORIGIN OF ANTIFERROMAGNETIC EXCHANGE

The antiferromagnetic nature of the exchange interaction between donor or acceptor states is a consequence of a direct exchange interaction between singly occupied distant orbitals; the interacting impurity spins prefer an antiferromagnetic coupling, since otherwise electrons cannot hop between orbitals to lower the kinetic energy due to the Pauli exclusion principle which prohibits two electrons with the same spin from residing at the same orbital. This argument can be simply expressed within the one-electron picture and confirmed for our specific case as in Fig. 4. First, the ferromagnetic case is explained schematically in Fig. 4(a). Before the intersite interaction is turned on between two impurity sites, spin-up and spin-down electron levels at each site are split by  $\Delta E_{\text{Zeeman}}$ due to the effective magnetic field applied to the two impurity atoms or due to an intra-atomic exchange interaction in the case of an intrinsically magnetic atom. The lower-energy majority-spin level in each atom, which is the spin-up state in Fig. 4(a), is occupied by one electron. When the intersite interaction is turned on between the sites, i.e., an electron can hop between the two impurity sites without flipping its spin, the original two impurity states form bonding and antibonding states. In this case, there is no energy gain by the intersite interaction because both the bonding and antibonding states are equally occupied by electrons. This schematic explanation is confirmed by observing the charge density distribution of bonding and antibonding states from our DFT calculation of the ferromagnetic spin configuration. In Fig. 4(c), we plot the squared amplitudes of wave functions  $[|\psi(\mathbf{r})|^2]$  of phosphorus doped Si NW along the wire axis. The squared amplitudes are averaged over the x and y directions and then plotted as a function of the z coordinate along the wire axis. The highest occupied molecular orbital (HOMO), which is associated with the antibonding state in Fig. 4(a), indeed has a large dip in the wave function amplitude between the two phosphorous atoms, which is a signature of an antibonding state, and the HOMO-1 state has enhanced wave function amplitude between the two phosphorus atoms consistent with the association with the bonding state in Fig. 4(a).

The situation is different for the antiferromagnetic case. Before the intersite interaction is turned on, the level splitting



FIG. 4. (Color online) Schematic level diagrams of intersite orbital interactions for (a) the ferromagnetic and (b) the antiferromagnetic spin alignments between two dopant atoms, and the squared amplitudes of wave functions of HOMO and HOMO-1 states as functions of the z coordinate (along the wire axis) in (c) and (d) for the two spin alignment cases, respectively. In (a) and (b), energy levels in black represent spin up states, while red is for spin down states. In (c) and (d), the squared amplitude of a wave function is averaged over the x and y directions, and also over the one primitive unit length in the z direction to damp out a rapidly oscillating component obscuring the shape of the overall charge distribution, which is the reason why the charge density dip between the two phosphorus atoms does not reach down to the zero value for the HOMO state in (c), as an antibonding state is expected to. In (c) and (d), the vertical red lines indicate positions of substitutional phosphorus atoms. Inset: a schematic energy level diagram for coupled phosphorus donors (a) in the bulk silicon (redrawn from Ref. [31]) and (b) in Si NWs where the quantum confinement effect increases the level spacing. The exchange interaction parameter J, which corresponds to the energy level difference between the two lowest energy levels, is enhanced in Si NWs compared with the bulk case.

between the spin-up and spin-down states at one impurity site is opposite to that at the other impurity site, so the intersite interaction between impurity states of the same spin results in the doubly degenerate bonding and antibonding states, as shown in Fig. 4(b). As the bonding states are occupied and the antibonding states are unoccupied, the intersite interaction produces a net energy gain, stabilizing the antiparallel spin arrangement over the parallel one. In this case, the asymmetric real-space distributions of HOMO and HOMO-1 wave functions over the two phosphorus atoms [Fig. 4(d)] are consistent with the bonding nature between impurity states with different energies as shown in Fig. 4(b).

#### VI. DISCUSSION

It should be noted here that there would be no static spontaneous magnetization around dopant atoms without the constraint given by the local effective magnetic field, as we already mentioned. Therefore, our results suggest that experimentally there is no static long-range magnetic order in phosphorus- or boron-doped Si NWs, and the spin coupling should be rather instantaneous in time and short ranged in space, in a form of magnetic fluctuations; thus our results of constrained DFT calculations can be considered as taking "snapshots" of instantaneous spin correlations. Actually this view is totally consistent with the original experimental report stating that the localized spins have arbitrary orientations with a local antiferromagnetic exchange interaction [32].

Our suggested mechanism of the exchange coupling between dopant orbitals in semiconductors is quite general and hence should hold true for general semiconductor systems, including the bulk silicon. With the dimensionality being reduced from bulk to NW, silicon can have several competing effects on the intersite exchange interaction between the impurity spins, which would either increase or decrease the interaction. On one hand, Si NWs have larger band gaps than the bulk silicon due to the quantum confinement, so the dielectric screening effect is expected to be weaker in Si NWs [44]. This would result in smaller effective Bohr radii of dopant impurity states; hence their overlap and subsequently the exchange interaction would be reduced at a given impurity-impurity distance compared with the bulk silicon case. On the other hand, for a given radius of impurity states, the overlap between the states should be enhanced in Si NWs compared with the bulk silicon when we consider an idealized argument that larger portions are overlapped between one-dimensional "spheres" (i.e., lines), than between three-dimensional spheres, for a given radius of the spheres and a distance between them. This would enhance the exchange interactions in Si NWs. Moreover, another important effect to consider is single-particle energy level configurations for the ground singlet and excited triplet states. A recent experimental work [31] indicates that the ground-state energy level for two coupled single donors is the bonding state between the  $A^1$ single donor states, while the first excited state  $(\tau_{e})$  is also a bonding combination of the triply degenerate T<sup>2</sup> single donor states for the bulk silicon, as shown schematically in the inset of Fig. 4. In the bulk silicon, spin-up and spin-down electrons occupy the lowest-energy  $\alpha_g$  state for the spin singlet state, while the lowest-energy  $\alpha_g$  state and the first excited state  $\tau_g$ would be occupied each by an electron with the same spin for the spin triplet state. In this case,  $J = E_T - E_S$  corresponds to the energy difference between the  $\alpha_g$  and  $\tau_g$  levels. In the meanwhile, for the Si NWs, the quantum confinement would increase the level spacing of the single donor states so that the  $\tau_g$  bonding state goes up above the  $\alpha_u$  antibonding level, increasing J. In fact, our first-principles calculation shows that two electrons occupy bonding and antibonding states for the spin triplet state, not two bonding states, as shown in Figs. 4(a) and 4(c). Overall, the exchange interaction is expected to be stronger in Si NWs than in bulk silicon as recently suggested by the experimental work [32,45].

# VII. CONCLUSIONS

In summary, we have investigated the nature of exchange interaction among substitutional phosphorous or boron dopants in Si NWs using the constrained DFT scheme. With applying a local effective magnetic field on a dopant, we have found that a local spin moment around the dopant induces a spin moment distribution around nearby impurity atoms with the opposite spin direction, indicating an antiferromagnetic exchange interaction. The calculated Heisenberg exchange parameter J is also antiferromagnetic, and its magnitude decreases monotonically with the increasing impurity-impurity distance. We have shown that the antiferromagnetic nature of the exchange interaction in this system can be understood within a simple model taking into account the effective hydrogenic impurity states of dopants and a direct exchange interaction between them to lower the electronic kinetic energy. Our result suggests a theoretical model for the recent experimental work [32] reporting the Kondo-like resistance dip as a function of temperature in heavily P-doped Si NWs.

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