

## Excitons and excitonic fine structures in Si nanowires: Prediction of an electronic state crossover with diameter changes

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Si nanowires have attracted considerable attention as promising candidates for electronic, thermoelectric, photonic, and photovoltaic devices, yet there appears to be only limited understanding of the underlying electronic and excitonic structures on all pertinent energy scales. Using atomistic pseudopotential calculations of single-particle as well as many-body states, we have identified remarkable properties of Si nanowires in three energy scales: (i) In the “high-energy”  $\sim 1$ -eV scale, we find an unusual electronic state crossover whereby the nature of the lowest unoccupied molecular orbital (LUMO) state changes its symmetry with wire diameters for [001]-oriented wires but not for [011]-oriented wires. This change leads to orbitally allowed transitions becoming orbitally forbidden below a certain critical diameter for [001] wires. (ii) In the “intermediate-energy”  $\sim 10^{-1}$ -eV scale, we describe the excitonic binding, finding that in [001] wires the diameter ( $D$ ) dependence of excitonic gap scales as  $1/D^{1.9}$ , not as  $1/D^1$  as expected. The exciton binding energy increases from 52 meV at  $D = 7.6$  nm to 85 meV at  $D = 3.3$  nm and 128 meV at  $D = 2.2$  nm. (iii) In the “low-energy”  $\sim 10^{-3}$ -eV scale, we describe dark/bright excitonic states and predict how orbitally allowed transitions [in scale (i)] become spin-forbidden due to the electron-hole exchange interaction, whereas the spin-allowed states in the orbitally forbidden diameter region remain dark. The diameter dependence of the fine-structure splitting of excitonic states scales as  $1/D^{2.3}$  in [001] wires and as  $1/D^{2.6}$  in [011] wires. Surface-polarization effects are found to significantly enhance electron-hole Coulomb interaction, but have a small effect on the exchange fine-structure splitting. The present work provides a road map for a variety of electronic and optical effects in Si nanowires that can guide spectroscopic studies.

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### I. INTRODUCTION

Si nanowires have attracted considerable interest as promising candidate structures for electronic,<sup>1,2</sup> thermoelectric,<sup>3,4</sup> photonic,<sup>5,6</sup> and photovoltaic devices,<sup>7–11</sup> reflected by numerous papers on growth,<sup>12–14</sup> structural characterization,<sup>15</sup> transport,<sup>16,17</sup> and optical<sup>15,18–23</sup> properties. Yet, there appears to be limited understanding of the underlying electronic and excitonic properties. Such understanding would span three energy scales: (i) in the high-energy  $\sim 1$ -eV scale one needs to understand the nature of confined energy levels and their dependence on wire orientation and diameter (single-particle physics); (ii) in the intermediate-energy  $\sim 10^{-1}$ -eV scale one needs to understand the screened electron-hole Coulomb attraction, which determines the exciton binding energy (many-body physics); and finally (iii) in the “low-energy”  $\sim 10^{-3}$ -eV scale one encounters the electron-hole exchange interaction, which splits the excitonic states into bright/dark states (many-body physics).

Current calculations and experiments on Si wires provide only limited understanding of the electronic and excitonic structures on all of these energy scales. On the theoretical side, in the  $\sim 1$ -eV energy scale (i), density-functional theory (DFT) calculations, which are computationally restricted to small-diameter wires, reported band structures for different wire orientations.<sup>24–27</sup> Since in DFT the bulk band gaps and effective masses are often underestimated (by 60%), the description of quantum confinement effects in nanowires is questionable. The semiempirical tight-binding method<sup>28</sup> was also used to probe scale (i). In the  $\sim 10^{-1}$ -eV energy scale (ii) the Bethe-Salpeter equation (BSE) within the GW method was used to describe excitonic absorption,<sup>29,30</sup> yet

GW-BSE calculations are computationally rather expensive, so large-diameter wires ( $> 1.5$  nm) were not considered and the spin-orbit (SO) coupling effect was generally ignored.<sup>29,30</sup> In the  $\sim 10^{-3}$ -eV energy scale (iii), the understanding is still dominated by the simple exchange singlet-triplet splitting model based on two single-particle levels.<sup>30,31</sup> Furthermore, in an indirect-gap system such as Si the dark states are not only exchange induced, but are affected by the symmetry of band-edge states and by intervalley coupling in the conduction bands.<sup>32,33</sup>

On the experimental side, scanning tunneling spectroscopy has been employed to evaluate the size-dependent quasiparticle band gaps in the scale (i). The gap increases from 1.1 eV at  $D = 7.0$  nm to 3.5 eV at  $D = 1.3$  nm.<sup>15</sup> As to scale (ii) and (iii), available photoluminescence spectra for Si nanowires show a complicated profile with relatively weak intensity compared to porous Si, broad peaks (the narrowest reported linewidth  $\nu \sim 85$  meV at 7 K),<sup>21</sup> and long carrier decay time on the order of  $1\text{--}10^3$   $\mu\text{s}$ .<sup>20,34</sup> These properties are strongly dependent on the wire size, morphology, and surface passivation.<sup>14,19,22,23</sup> In this situation theoretical studies on excitonic properties of Si wires were usually compared to experimental results for porous Si,<sup>29,30</sup> which has a yet poorly understood morphology and interface.

Here we describe via explicit atomistic pseudopotential calculations a comprehensive analysis of Si nanowires along the [001] and [011] growth direction on all three energy scales. In scale (i) we find an unusual electronic state crossover whereby the nature of the lowest unoccupied molecular orbital (LUMO) state changes its symmetry with wire diameter for [001] wires but not for [011]. This symmetry change leads

to orbitally allowed transitions becoming orbitally forbidden below a certain critical diameter for [001] wires. In scale (ii) we describe the excitonic states of Si wires for different sizes and orientations, predicting the symmetry and polarization of the first few excitonic peaks. In [001] wires, the electronic state crossover noted above leads to distinct polarization behaviors of excitons for different diameter regions, whereas for [011] wires the excitonic structure is much simpler and the bright exciton is always polarized along the wire growth direction. In scale (iii) we predict how orbitally allowed transitions [in scale (i)] become spin-forbidden due to the electron-hole exchange interaction, whereas spin-allowed states in the orbitally forbidden diameter region are still dark. We also discussed the effect of surface polarization induced by the dielectric mismatch between Si wire and the surrounding material. This study provides a road map for a variety of optical effects in Si nanowires that can guide spectroscopic studies of such systems.

## II. METHOD

The single-particle electronic energies and wave functions [scale (i)] are calculated via the atomistic pseudopotential method described in Ref. 35. Briefly, the nanowire system is described by solving the Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + \sum_{n,\alpha} v_\alpha(\mathbf{r} - \mathbf{R}_{n,\alpha}) + \sum_\alpha V_\alpha^{SO} \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (1)$$

where the Hamiltonian consists of the kinetic energy (first term), the nanocrystal potential (second term), and the spin-orbit operator (third term). The nanocrystal potential specifies the atomistic symmetry as well as the mesoscopic shape and size of nanostructures, and is represented as a superposition of screened atomic pseudopotentials  $v_\alpha(\mathbf{r} - \mathbf{R}_{n,\alpha})$  centered at the atom sites  $\mathbf{R}_{n,\alpha}$ .  $v_\alpha(\mathbf{r} - \mathbf{R}_{n,\alpha})$  and  $V_\alpha^{SO}$  are fitted to accurately reproduce the properties of bulk Si (band gap, critical energy

levels, effective masses, deformation potentials, and spin-orbit splittings), thus correcting the well-known ‘‘DFT errors’’ for semiconductors. The Hamiltonian is diagonalized iteratively by expanding the wave function [ $\psi_i(\mathbf{r})$  in Eq. (1)] in plane waves, and selectively calculating band-edge states via the folded spectrum method.<sup>36,37</sup> The pseudopotential method naturally includes the effects of atomistic symmetry, quantum confinement, spin-orbit coupling, multiband coupling, and intervalley coupling (the last two originating from the lack of translational symmetry in nanostructures). Here the Si wires are constructed with circular cross sections (except as noted) along the [001] and [011] direction and are embedded in a matrix material having a (variable) wide gap, mimicking various target surface passivations. Whereas other specific passivations have been used in the literature such as atomistic hydrogen H termination, we prefer here to capture a range of possible passivations by using a generic one.

The many-body excitonic properties [scales (ii) and (iii) above] are calculated within the framework of the screened configuration-interaction (CI) approach.<sup>38</sup> The exciton wave functions  $|\Theta^{(v)}\rangle$  are expanded in terms of linear combinations of Slater determinants  $|\Phi_{h_i,e_j}\rangle$  (corresponding to the  $h_i$ - $e_j$  electron-hole pair) constructed from the antisymmetrized products of single-particle wave functions  $\psi_i(\mathbf{r})$  obtained from Eq. (1):

$$|\Theta^{(v)}\rangle = \sum_{h_i,e_j} C^{(v)}(h_i,e_j) |\Phi_{h_i,e_j}\rangle, \quad (2)$$

where the coefficients  $C^{(v)}(h_i,e_j)$  are the eigenstates of the CI Hamiltonian constructed by using the electron-hole Coulomb ( $J_{h_i e_j, h'_i e'_j}$ ) and exchange ( $K_{h_i e_j, h'_i e'_j}$ ) integrals:

$$\begin{aligned} H_{h_i e_j, h'_i e'_j} &\equiv \langle \Phi_{h_i, e_j} | H_{CI} | \Phi_{h'_i, e'_j} \rangle \\ &= (\epsilon_{e_j} - \epsilon_{h_i}) \delta_{h_i h'_i} \delta_{e_j e'_j} - J_{h_i e_j, h'_i e'_j} + K_{h_i e_j, h'_i e'_j}. \end{aligned} \quad (3)$$

The eigenvalues are energies of excitons,  $E_X$ . The  $J_{h_i e_j, h'_i e'_j}$  and  $K_{h_i e_j, h'_i e'_j}$  are calculated by using the single-particle orbitals  $\psi_i(\mathbf{r})$ :

$$J_{h_i e_j, h'_i e'_j} = e^2 \sum_{\sigma_1, \sigma_2} \iint \frac{\psi_{h'_i}^*(\mathbf{r}_1, \sigma_1) \psi_{e'_j}^*(\mathbf{r}_2, \sigma_2) \psi_{h_i}(\mathbf{r}_1, \sigma_1) \psi_{e_j}(\mathbf{r}_2, \sigma_2)}{\bar{\epsilon}(\mathbf{r}_1, \mathbf{r}_2) |\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

$$K_{h_i e_j, h'_i e'_j} = e^2 \sum_{\sigma_1, \sigma_2} \iint \frac{\psi_{h'_i}^*(\mathbf{r}_1, \sigma_1) \psi_{e'_j}^*(\mathbf{r}_2, \sigma_2) \psi_{e'_j}(\mathbf{r}_1, \sigma_1) \psi_{h_i}(\mathbf{r}_2, \sigma_2)}{\bar{\epsilon}(\mathbf{r}_1, \mathbf{r}_2) |\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (5)$$

The screening for these integrals is described by a position-dependent and size-dependent screening function  $\bar{\epsilon}(\mathbf{r}_1, \mathbf{r}_2)$ , which gives a physically smooth transition from short range (unscreened) to long range (screened).<sup>38</sup> To describe the electron-hole interaction for excitons, in the CI calculations the wires are periodically expanded along the growth direction with a length of  $\sim 11$  nm, which is more than twice the exciton Bohr radius of bulk Si ( $\sim 4.9$  nm). We use a large enough number of single-particle valence ( $>40$ ) and conduction ( $>40$ ) -band states to converge our CI basis: the calculated excitonic

energies  $E_X$  have a residual convergence error of less than 0.2 meV.

The optical-absorption spectra including excitonic effect are calculated with the CI eigenstates of Eq. (3) by using Fermi's golden rule:

$$I(E) = \sum_v |\mathbf{M}_v|^2 \exp \left[ - \left( \frac{E - E_v}{\sigma} \right)^2 \right], \quad (6)$$

where  $\mathbf{M}_v = \sum_{h_i, e_j} C^{(v)}(h_i, e_j) \langle \psi_{h_i} | \hat{\mathbf{P}} | \psi_{e_j} \rangle$  is the dipole transition matrix,  $E_v$  is the exciton energy and the broadening of spectral lines,  $\sigma$  is chosen as  $50 \mu\text{eV}$ . The exciton decay lifetime ( $\tau_v$ ) is calculated according to<sup>39</sup>

$$\frac{1}{\tau_v} = \frac{4\alpha E_v n |M_v|^2}{m_0^2 \hbar c^2}, \quad (7)$$

where  $n$  is the refractive index ( $\sim 4.0$  for photon energies of 1–2 eV for Si),<sup>40</sup>  $\alpha$  is the fine-structure constant,  $m_0$  is the electron rest mass, and  $c$  is the velocity of light.

The dielectric mismatch between the nanostructure (dielectric constant  $\epsilon_{\text{in}}$ ) and its surrounding material ( $\epsilon_{\text{out}}$ ) will create image charges at the surface.<sup>41</sup> This leads to two additional contributions to the energies of excitons: (i) the self-energy correction ( $\Sigma_i^{\text{pol}}$ ) of an electron (hole) in the single-particle state  $i$ , originating from the interaction between the electron (hole) and its own image charge; (ii) the Coulomb (exchange) interaction correction ( $U_{h_i e_j, h'_i e'_j}^{\text{pol}}$ ), originating from the mutual interaction of electron and hole, mediated by their

image charges. The self-energy term is evaluated in first-order perturbation theory by

$$\Sigma_i^{\text{pol}} = \int |\psi_i(\mathbf{r})|^2 \Sigma(\mathbf{r}) d\mathbf{r}, \quad (8)$$

where  $\psi_i(\mathbf{r})$  is the single-particle wave function from Eq. (1) and the surface-polarization potential,  $\Sigma(\mathbf{r})$  is numerically calculated as in Ref. 42. The Coulomb (exchange) interaction term is calculated via the electrostatic potential,  $\Omega_{e_j, e'_j}^{\text{pol}}(\mathbf{r})$ ,

$$U_{h_i e_j, h'_i e'_j}^{\text{pol}} = e^2 \sum_{\sigma} \int \psi_{h_i}^*(\mathbf{r}, \sigma) \psi_{h'_i}(\mathbf{r}, \sigma) \Omega_{e_j, e'_j}^{\text{pol}}(\mathbf{r}) d\mathbf{r}, \quad (9)$$

where  $\Omega_{e_j, e'_j}^{\text{pol}}(\mathbf{r})$  is the solution of the generalized Poisson equation,

$$\begin{aligned} \nabla \cdot \epsilon(\mathbf{r}) \nabla [\Omega_{e_j, e'_j}^{\text{dir}}(\mathbf{r}) + \Omega_{e_j, e'_j}^{\text{pol}}(\mathbf{r})] \\ = -4\pi e^2 \sum_{\sigma} \psi_{e_j}^*(\mathbf{r}, \sigma) \psi_{e'_j}(\mathbf{r}, \sigma), \end{aligned} \quad (10)$$

where the macroscopic dielectric constant  $\epsilon(\mathbf{r})$  changes smoothly from  $\epsilon_{\text{in}}$  to  $\epsilon_{\text{out}}$  at the wire surface.  $\Omega_{e_j, e'_j}^{\text{dir}}(\mathbf{r})$

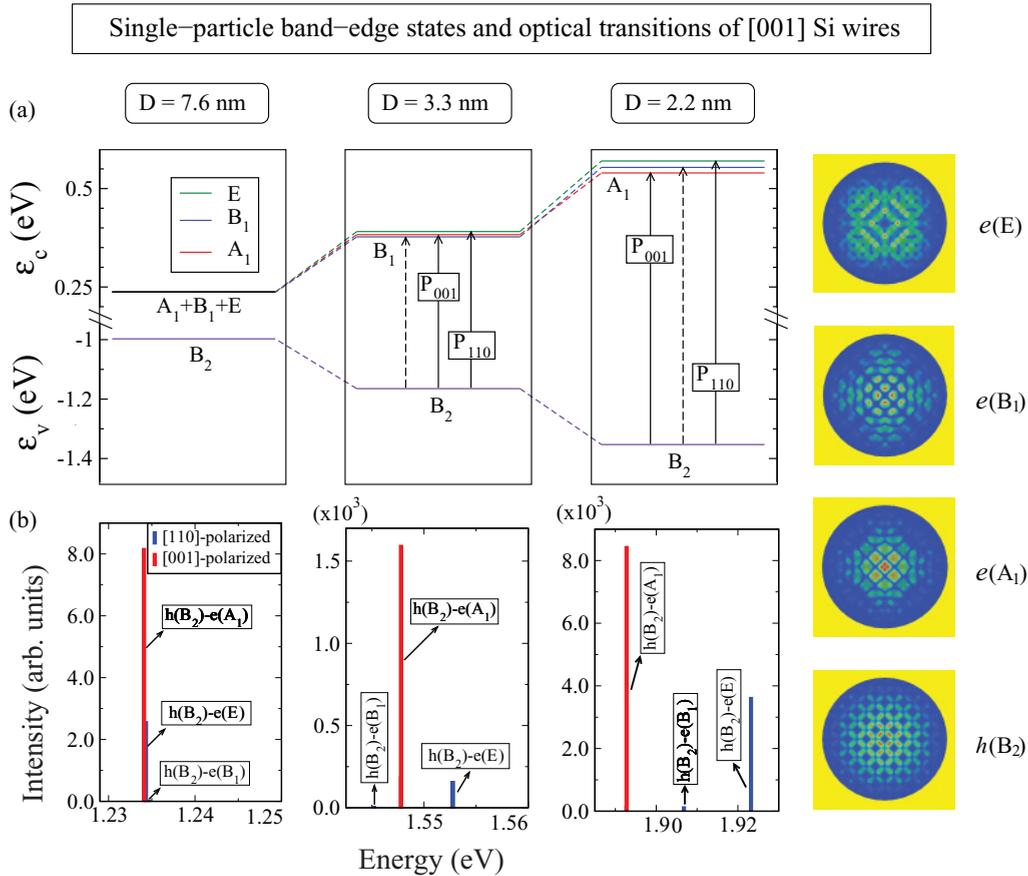


FIG. 1. (Color online) Single-particle band-edge energy levels (a), wave function amplitudes (right panel), and corresponding optical transitions (b) for [001] Si wires of diameter  $D = 7.6, 3.3,$  and  $2.2$  nm. These diameters are chosen to represent three distinct size regimes with different optical transitions. The square of wave functions are shown for a  $D = 3.3$  nm wire, with the plane intersecting the wire, perpendicular to the wire axis. The wire cross sections are shown as blue circles. The dashed arrow lines represent orbitally forbidden transitions whereas the solid arrow lines correspond to orbitally allowed transitions. Note that as a result of strong confinement, the oscillator strength for  $D = 3.3$  and  $2.2$  nm are enhanced by two orders of magnitude compared with that for  $D = 7.6$  nm.

TABLE I. Direct product of interband dipole matrix elements  $\langle h|\mathbf{P}_i|e\rangle$  in Si [001] wires ( $D_{2d}$  symmetry) and [011] wires ( $C_{2v}$  symmetry).  $\mathbf{P}_i$  represents the dipole operator along the wire axis ( $P_{001}$  for [001] wires and  $P_{011}$  for [011] wires) and in-plane direction ( $P_{110}$  for [001] and  $P_{100}$  for [011]). The symmetric  $A_1$  representation (dipole-allowed transition) is given in bold. For [001] wires the LUMO  $A_1$  is allowed in  $P_{001}$  and  $E$  is allowed in  $P_{110}$ . For [011] wires  $A_1$  is allowed in  $P_{011}$ .

[001]:	$\langle h P_{001}(B_2) e\rangle$	$\langle h P_{110}(E) e\rangle$
	$\langle B_2 \otimes B_2 \otimes A_1 \rangle = \mathbf{A}_1$	$\langle B_2 \otimes E \otimes A_1 \rangle = E$
	$\langle B_2 \otimes B_2 \otimes B_1 \rangle = B_1$	$\langle B_2 \otimes E \otimes B_1 \rangle = E$
	$\langle B_2 \otimes B_2 \otimes E \rangle = E$	$\langle B_2 \otimes E \otimes E \rangle =$ $\mathbf{A}_1 \oplus A_2 \oplus B_1 \oplus B_2$
[011]:	$\langle h P_{011}(B_1) e\rangle$	$\langle h P_{100}(A_1) e\rangle$
	$\langle B_1 \otimes B_1 \otimes A_1 \rangle = \mathbf{A}_1$	$\langle B_1 \otimes A_1 \otimes A_1 \rangle = B_1$

corresponds to the electrostatic potential excluding the surface-polarization effect, and is the solution of the Poisson equation,

$$\epsilon(\mathbf{r})\nabla^2\Omega_{e_j,e'_j}^{\text{dir}}(\mathbf{r}) = -4\pi e^2 \sum_{\sigma} \psi_{e'_j}^*(\mathbf{r},\sigma)\psi_{e_j}(\mathbf{r},\sigma). \quad (11)$$

Equations (10) and (11) are solved in real space by using a finite-difference discretization of the gradient operator and a conjugate-gradient minimization algorithm.<sup>42,43</sup>

In the following we first present results for [001] wires from the above (i), (ii), and (iii) energy scales, and then show results for [011] wires. We then discuss the effects of dielectric mismatch on exciton binding and exchange interaction.

#### A. The $eV$ energy scale: Single-particle states

Bulk Si has six equivalent conduction-band valleys  $\Delta_X$  (along the  $\Gamma$ - $X$  direction), from which the LUMO of wires is derived. The confinement plane of [001] wires contains four of these six  $\Delta_X$  valleys, folded to the  $\bar{\Gamma}$  point of the wire Brillouin zone. For [001] wires belonging to the  $D_{2d}$  point group, symmetry analysis<sup>44</sup> indicates that these four  $\Delta_X$ -derived states correspond to the  $A_1$ ,  $B_1$ , and  $E$  representation, where both  $A_1$  and  $B_1$  are nondegenerate and  $E$  is doubly degenerate. The highest occupied molecular orbital (HOMO) always has nondegenerate  $B_2$  symmetry for all wire sizes. Figures 1(a) and 2 show evolution of the LUMO and HOMO state when the wire diameter is varied. At large diameter  $D = 7.6$  nm, as quantum confinement and intervalley coupling are negligible, the splitting between  $A_1$ ,  $B_1$ , and  $E$  is tiny, leaving all these states practically degenerate. With decreasing diameters, the enhanced intervalley coupling lifts the degeneracy of these four states. This makes the  $B_1$  state the lowest-energy one at diameter  $D = 3.3$  nm to  $D \sim 2.5$  nm (see Fig. 2). For lower diameters, the  $A_1$  state becomes the LUMO [e.g.,  $D = 2.2$  nm in Fig. 1(a)]. In contrast to the LUMO, the HOMO keeps the  $B_2$  symmetry for all the diameters. These HOMO and LUMO states have characteristic wave functions corresponding to their specific symmetries, as shown in the right part of Fig. 1.

The switching of symmetry of the LUMO state with diameter has a strong effect on the optical properties of these wires. Table I shows the direct product  $\langle h|\mathbf{P}_i|e\rangle$  for electron-hole dipole transition matrix elements, in terms of the irreducible

representations of the  $D_{2d}$  group ( $|e\rangle = A_1; B_1; E$  and  $|h\rangle = B_2$ ). The dipole operator  $\mathbf{P}_i$  consists of two components:  $P_{001}$  representing photon polarized along the wire axis (along wire), belonging to  $B_2$  representation and  $P_{110}$  representing photon polarized perpendicular to the wire axis (in plane), belonging to  $E$  representation. Any direct product having a symmetric  $A_1$  representation is orbitally allowed.<sup>45</sup> Thus among all the HOMO $\rightarrow$ LUMO transitions for [001] wires,  $B_2 \rightarrow A_1$  with the photon polarization  $P_{001}$  (along wire) and  $B_2 \rightarrow E$  with  $P_{110}$  (in plane) are orbitally allowed, whereas  $B_2 \rightarrow B_1$  is orbitally forbidden. This symmetry analysis is consistent with our numerical calculations of the oscillator strength depicted in Fig. 1(b). At diameter  $D = 7.6$  nm, we can see both  $B_2 \rightarrow A_1$  (along-wire polarized) and  $B_2 \rightarrow E$  (in-plane polarized) transitions are orbitally allowed, whereas the  $B_2 \rightarrow B_1$  transition is orbitally forbidden. With decreasing diameters, the LUMO symmetry changes from degenerate  $A_1 + B_1 + E$  (at  $D = 7.6$  nm) to  $B_1$  (at  $D = 3.3$  nm) and finally to  $A_1$  (at  $D = 2.2$  nm). The optical transitions [Fig. 1(b)] show corresponding changes in polarization. At  $D = 3.3$  nm the orbitally forbidden  $B_2 \rightarrow B_1$  transition is below the orbitally allowed  $B_2 \rightarrow A_1$  and  $B_2 \rightarrow E$  transitions, and then at  $D = 2.2$  nm the orbitally allowed  $B_2 \rightarrow A_1$  transition emerges as the lowest-energy one with along-wire polarization. We also checked the above calculations for wires with square cross section (also belonging to the  $D_{2d}$  point group) and obtain exactly the same symmetry-change sequence for the LUMO state. This indicates that the symmetry change does not depend on slight modifications of the wire surface. It is an intrinsic property of the wire  $D_{2d}$  symmetry, which originates from the competition between quantum confinement and intervalley coupling. *Thus we predict a confinement-induced electronic state crossover with diameter changes in [001] Si wires.* As shown below, this will result in corresponding transitions between different excitonic states.

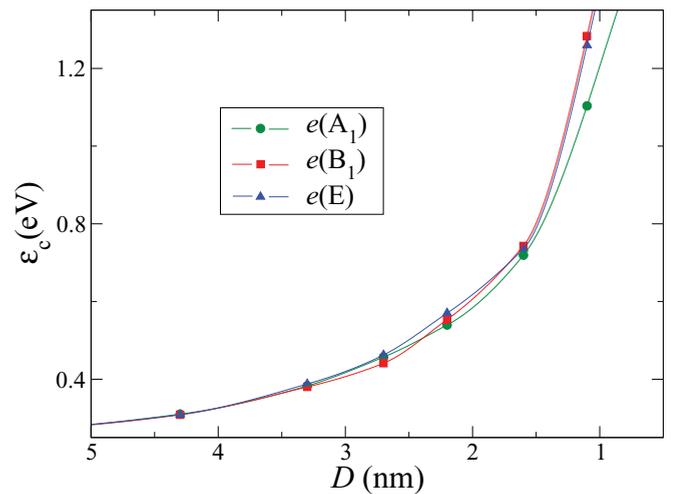


FIG. 2. (Color online) Evolution of energies and symmetries of conduction-band-edge states with decreasing diameters in Si [001] wires. One can clearly see the symmetry change sequence of the LUMO state with decreasing diameters: from degenerate  $A_1 + B_1 + E$  to  $B_1$ , and to  $A_1$ .

TABLE II. Symmetry analysis of the excitonic states generated from HOMO and LUMO single-particle orbitals of [001] and [011] Si wires. Single-group representations are converted to corresponding double-group representations to include the spin degree of freedom for excitons.

	HOMO	LUMO	Excitons (HOMO $\otimes$ LUMO)
<b>[001]:</b>			
$D = 7.6$ nm	$B_2 \rightarrow \Gamma_6$	$E \rightarrow \Gamma_6 + \Gamma_6$	$\Gamma_6 \otimes \Gamma_6 = A_1 \oplus A_2 \oplus E$
$D = 3.3$ nm	$B_2 \rightarrow \Gamma_6$	$B_1 \rightarrow \Gamma_6$	$\Gamma_6 \otimes \Gamma_6 = A_1 \oplus A_2 \oplus E$
$D = 2.2$ nm	$B_2 \rightarrow \Gamma_6$	$A_1 \rightarrow \Gamma_7$	$\Gamma_6 \otimes \Gamma_7 = B_1 \oplus B_2 \oplus E$
<b>[011]:</b>			
$D = 3.3$ nm	$B_1 \rightarrow \Gamma_5$	$A_1 \rightarrow \Gamma_5$	$\Gamma_5 \otimes \Gamma_5 = A_1 \oplus A_2 \oplus B_1 \oplus B_2$

### B. Intermediate energy scale: Excitonic states

Based on the group theory Table II describes how single-particle HOMO and LUMO states contribute to produce excitons. Here we convert single-group representations to corresponding double-group ones adding the spin degrees of freedom. It can be seen that three groups of excitonic states emerge from different symmetry of the LUMO state:

(1) At diameter  $D = 7.6$  nm [Fig. 3(a)], the spin-orbit interaction splits the doubly degenerate LUMO  $E$  to  $\Gamma_6 + \Gamma_6$ , and also transforms the HOMO  $B_2$  to  $\Gamma_6$ . This  $\Gamma_6 \otimes \Gamma_6$  manifold in principle should lead to two combinations of  $A_1 \oplus A_2 \oplus E$  excitonic states, of which the doubly degenerate  $E$  state is bright and in-plane polarized. However, due to very weak splitting of the two  $\Gamma_6$  states (as a result of weak

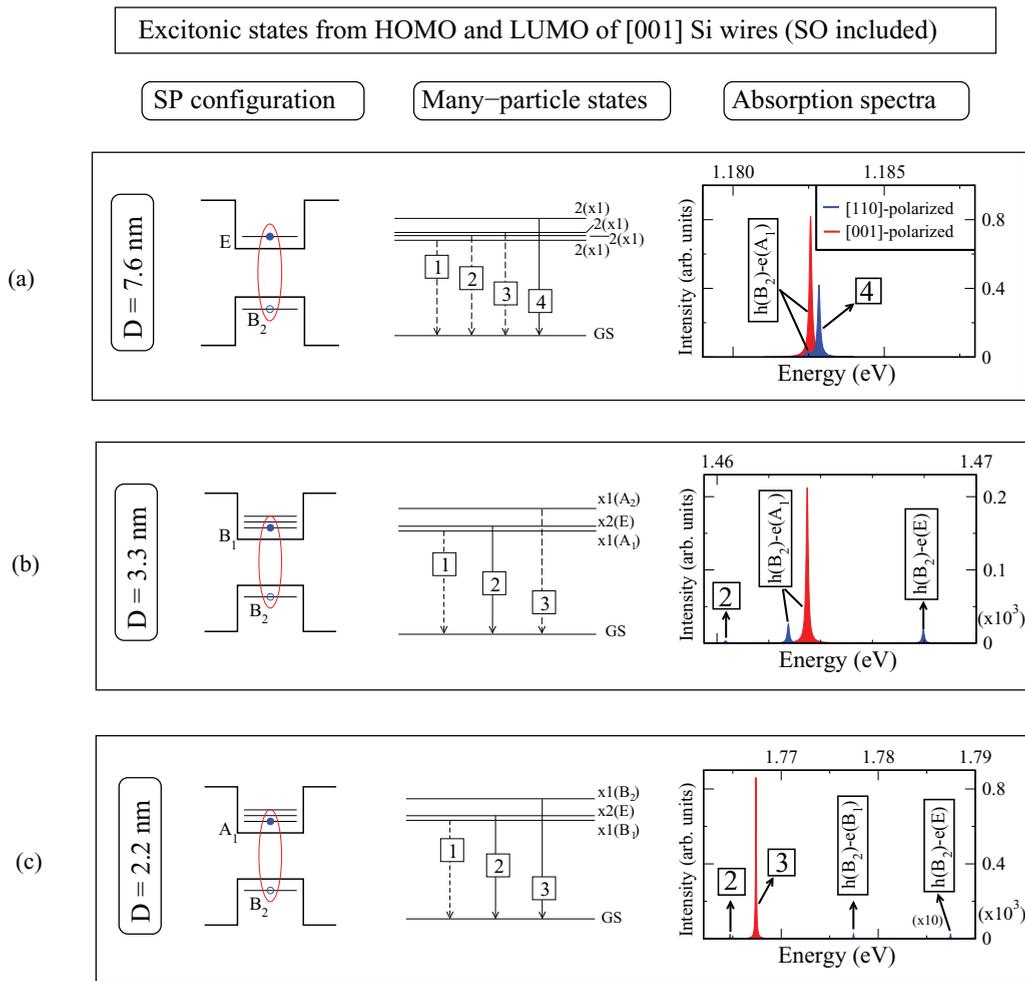


FIG. 3. (Color online) Many-body excitonic states generated from HOMO $\otimes$ LUMO and absorption spectra for [001] Si wires at  $D = 7.6$  (a), 3.3 (b), and 2.2 nm (c). The effect of spin-orbit coupling is included. Dashed arrow lines represent spin-forbidden transitions whereas solid arrow lines represent spin-allowed transitions. The GS refers to the ground state after electron-hole recombination. The notations 1, 2, 3, and 4 mean the order of excitonic transitions from lower energy to higher energy in individual exciton group. The transition 1 corresponds to the ground excitonic state (excitonic gap).

TABLE III. Calculated ground-state exciton energy  $E(i)$  and exciton fine-structure splittings for [001] wires (Fig. 3) and [011] wires (Fig. 6).  $E(i)$  ( $i = 1, 2, 3$ , and 4) represent the energy of excitonic transition corresponding to the notation (1, 2, 3, and 4) in Figs. 3 and 6.

$D$ (nm)	[001]:			[011]:
	7.6	3.3	2.2	3.3
$E(1)$ (eV)	1.182	1.460	1.764	1.335
$E(2)-E(1)$ ( $\mu\text{eV}$ )	21.3	238.9	399.4	3.4
$E(3)-E(2)$ ( $\mu\text{eV}$ )	25.1	721.3	2668.6	20.8
$E(4)-E(3)$ ( $\mu\text{eV}$ )	92.4			1017.6

SO coupling), there is strong configuration mixing between these two  $\Gamma_6 \otimes \Gamma_6$  exciton combinations, resulting in six lower-energy dark excitonic states and two upper bright states (in-plane polarized, labeled as transition 4) as described in Fig. 3(a).<sup>46</sup>

(2) At diameter  $D = 3.3$  nm [Fig. 3(b)], the LUMO  $B_1$  state is transformed to  $\Gamma_6$ , leading to  $\Gamma_6 \otimes \Gamma_6 = A_1 \oplus A_2 \oplus E$  excitonic states. The middle  $E$  state (labeled as transition 2) is bright with in-plane polarization.

(3) At diameter  $D = 2.2$  nm [Fig. 3(c)], the LUMO  $A_1$  state becomes  $\Gamma_7$ . When combined with the HOMO  $\Gamma_6$ , it generates the exciton combination  $B_1 \oplus B_2 \oplus E$ . The top  $B_2$  (labeled as transition 3) and middle  $E$  state (labeled as transition 2) are bright with along-wire and in-plane polarization, respectively.

The calculated energy of the ground excitonic state [the lowest eigenvalue of Eq. (3)],  $E_X$  are 1.182, 1.460, and 1.764 eV for  $D = 7.6$  nm ( $B_2 \rightarrow E$ ), 3.3 nm ( $B_2 \rightarrow B_1$ ), and 2.2 nm ( $B_2 \rightarrow A_1$ ), respectively, as the  $E(1)$  listed in Table III. We fit the size dependence of  $E_X$  according to

$$E_X = E_X^{\text{bulk}} + \frac{a}{D^\lambda}, \quad (12)$$

where  $E_X^{\text{bulk}} = 1.1552$  eV,<sup>40</sup> and  $D$  is the diameter, finding  $a = 2.75$  and  $\lambda = 1.90$ . As expected from quantum confinement, the exciton binding energy (the energy difference between the quasiparticle band gap and the ground-state excitonic energy) is significantly enhanced from bulk Si ( $\sim 15$  meV) (Ref. 47) to Si wires, giving 52 meV (at  $D = 7.6$  nm), 85 meV ( $D = 3.3$  nm), and 128 meV ( $D = 2.2$  nm).

### C. Low $10^{-3}$ -eV energy scale: Bright/dark states vs fine-structure splittings

The absorption spectra shown on the right-hand side of Fig. 3 describe the bright/dark excitonic states caused by the exchange interaction and the intervalley coupling. For narrow wire of diameter  $D = 2.2$  nm, the ground-state excitons originate from the orbitally allowed  $B_2 \rightarrow A_1$  transition. The lowest one ( $B_1$  symmetry) is dark (spin forbidden), and higher states are spin allowed — the middle semibright state ( $E$ , in-plane polarized) and the highest bright state ( $B_2$ , along-wire polarized). For medium wire of diameter  $D = 3.3$  nm, the orbitally forbidden  $B_2 \otimes B_1$  is lower in energy than the other two orbitally allowed combinations  $B_2 \otimes A_1$  and  $B_2 \otimes E$  and

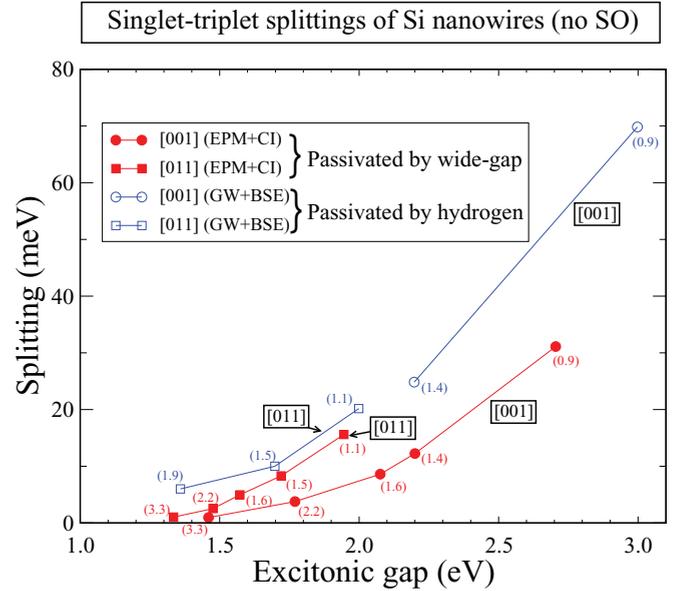


FIG. 4. (Color online) Calculated excitonic-gap dependence of the singlet-triplet splitting  $\Delta_{ST}$  (without including spin-orbit coupling) in Si [001] and [011] wires, compared to GW + BSE results (Ref. 30). The wire diameter value is marked onto individual data point. For same-diameter points, we construct the same wire cross section as Ref. 30 (not circular), while for larger diameter wires we use the circular cross sections.

contributes to the ground-state excitons. In these excitons, the lowest ( $A_1$ ) and highest ( $A_2$ ) states are spin forbidden and only the middle one ( $E$ ) is spin allowed. However, even this spin-allowed state is generally dark, because it is orbitally forbidden. At wide wire of diameter  $D = 7.6$  nm, the bright in-plane polarized peak (labeled as transition 4) comes from the  $B_2 \rightarrow E$  transition, which gives two spin-allowed excitons at the highest energy as mentioned. Also the exciton groups corresponding to  $B_2 \rightarrow A_1$  and  $B_2 \rightarrow B_1$  (all dark states) appear as ground-state excitons owing to the degeneracy of the LUMO state. The absorption spectrum of  $D = 3.3$  [Fig. 3(b)] and 2.2 nm [Fig. 3(c)] also shows the excited excitonic states at higher energies, which can be attributed to  $B_2 \rightarrow (A_1/B_1/E)$  transitions.

The calculated exciton fine-structure splittings are listed in Table III. These are quite distinct from the results on Si quantum dots,<sup>32</sup> due to different degeneracy and symmetry of the LUMO and HOMO states. Figure 4 shows the excitonic-gap dependence of the singlet-triplet splitting with no SO,  $\Delta_{ST}$ , compared with previous GW+BSE results.<sup>30</sup> The wire diameter dependence of  $\Delta_{ST}$  is found to scale as  $1/D^{2.3}$ . Previous GW+BSE calculations show much larger excitonic-gap energies and exchange splittings than ours at the same diameters, especially for the [001] wires. This could result from a high hydrogen coverage (high H-to-Si ratio) in their narrow wires: e.g., they used  $\text{Si}_{25}\text{H}_{20}$  at  $D = 0.9$  nm and  $\text{Si}_{49}\text{H}_{28}$  at  $D = 1.4$  nm for [001] wires.<sup>29</sup> The (cluster-connected) [001] wires require more H than (linear-chain-like) [011] wires,<sup>27</sup> and thus their electronic and excitonic properties are affected more by H passivation than those of [011] wires. The Si-H bonding is known to modify Si enormously and H passivation has been reported to result in much bigger

band gaps than those with other passivations.<sup>48</sup> In the present work, the wire surfaces are passivated by generic large band-gap materials, and much larger diameter wires can be calculated.

We calculate the exciton decay time ( $\tau_v$ ) for the bright excitonic states. At  $D = 3.3$  nm,  $\tau_v$  of the transition 2 [Fig. 3(b)] is 1963.7  $\mu$ s, as expected from its low oscillator strength since it is orbitally forbidden (though spin allowed). At  $D = 2.2$  nm,  $\tau_v$  of transition 2 and transition 3 [Fig. 3(c)] are 77.2 and 1.6  $\mu$ s. The long decay time is consistent with pseudodirect band-gap character of Si nanostructures and are reasonably within the range of experimentally measured 1–10<sup>3</sup>  $\mu$ s.<sup>20,34</sup>

### III. RESULTS FOR [011] WIRES

In [011] wires having the  $C_{2v}$  point-group symmetry, two of the six equivalent bulk valleys  $\Delta_X$  are projected to the confinement plane, and thus at large diameters the LUMO consists of only two degenerate states. In contrast to [001] wires, both of them belong to the  $A_1$  representation, and thus no symmetry change of the LUMO state occurs with varying diameters. Figure 5 shows the single-particle states and related optical transitions at  $D = 3.3$  nm, and Table I gives the symmetry analysis of dipole matrix elements. Despite having the same symmetry, the two  $A_1$  electron states show different wave functions. The HOMO has the  $B_1$  symmetry, and thus all interband transitions ( $B_1 \rightarrow A_1$ ) have along-wire polarization,  $P_{011}$  (Table I), as also confirmed by the calculated optical absorptions in Fig. 5(b).

Figure 6 shows the excitonic structures generated from the HOMO and LUMO state. The corresponding symmetry analysis are given in Table II. The HOMO  $\Gamma_5$  (from  $B_1$ )

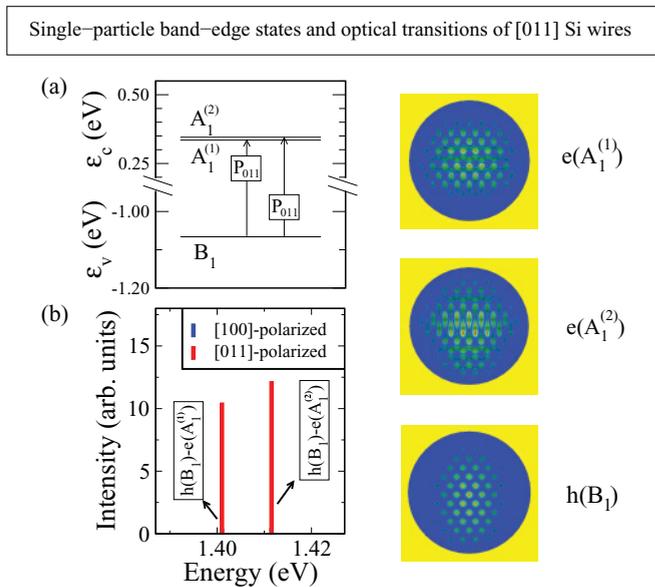


FIG. 5. (Color online) Single-particle band-edge energy levels (a), corresponding optical transitions (b), and wave function amplitudes (right panel) for [011] Si wires of diameter  $D = 3.3$  nm. The asymmetry of wave functions originate from the fact that the  $x$  and  $y$  directions of [011] wires are not equivalent, thus resulting in different confinement behaviors.

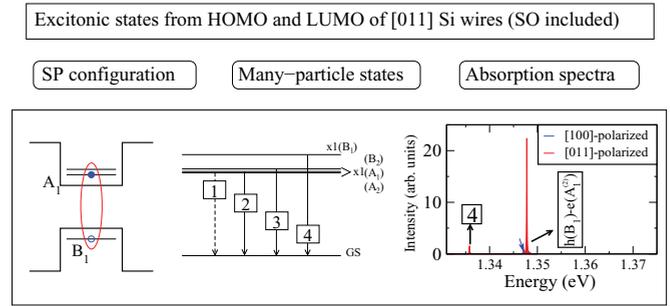


FIG. 6. (Color online) Many-body excitonic structure and absorption spectrum generated from HOMO $\otimes$ LUMO for [011] Si wires of diameter  $D = 3.3$  nm.

state and LUMO  $\Gamma_5$  (from  $A_1$ ) state produce the exciton combination of  $A_1 \oplus A_2 \oplus B_1 \oplus B_2$ . Among them the  $B_1$  is a bright state with along-wire polarization, and  $A_1, B_2$  are also bright with in-plane polarization. However, in the absorption spectra of Fig. 6 (right panel) we only can observe the bright  $B_1$  exciton (labeled as transition 4) with the along-wire polarization, as the semidark  $A_1$  (transition 2) and  $B_2$  (transition 3) have two-order smaller oscillator strength. The ground-state excitonic energy is 1.335 eV (Table III) and the corresponding exciton binding energy is 66 meV. Both are smaller than those of the same size [001] wire due to weaker confinement. The fine-structure splittings for the  $B_1 \rightarrow A_1^{(1)}$  exciton group are listed in Table III. The excitonic-gap dependence of exchange splitting  $\Delta_{ST}$  is shown in Fig. 4. The diameter dependence of  $\Delta_{ST}$  scales as  $1/D^{2.6}$ , i.e., with a larger scaling factor than that of [001] wires. The calculated exciton decay time of the bright 4 state in Fig. 6 is 20.9  $\mu$ s.

### IV. EFFECTS OF DIELECTRIC MISMATCH

Because nanowires are usually surrounded by materials with small dielectric constants (e.g., air, water, oxides, and organics), we studied the effects of dielectric mismatch by

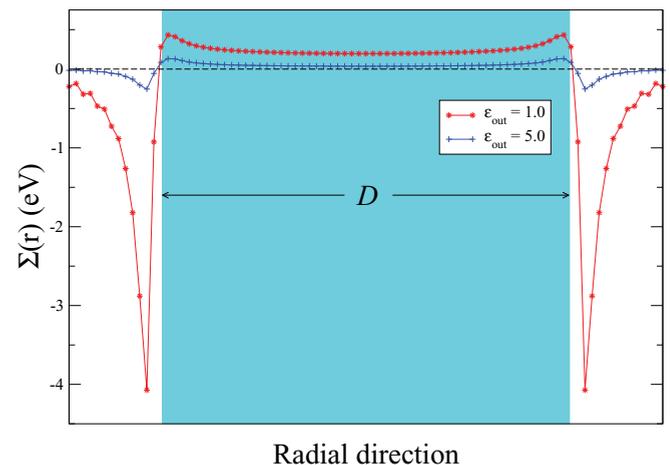


FIG. 7. (Color online) The numerically calculated surface-polarization potential  $\Sigma(r)$  of a Si wire ( $D = 3.3$  nm) is shown along the radial direction, for two values of macroscopic dielectric constant of the surrounding material ( $\epsilon_{\text{out}} = 1.0, 5.0$ ).

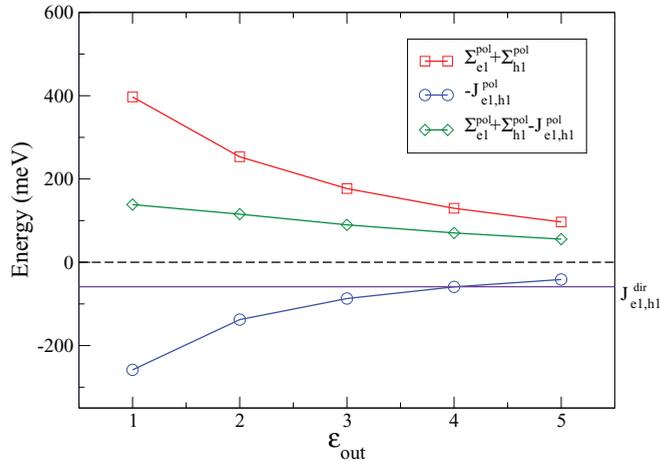


FIG. 8. (Color online) The surface-polarization-induced self-energy,  $\Sigma_i^{pol}$  [ $i = e1$  (LUMO) and  $h1$  (HOMO)], Coulomb interaction  $-J_{e1,h1}^{pol}$  (negative value means decreasing exciton energies), and the sum  $\Sigma_{e1}^{pol} + \Sigma_{h1}^{pol} - J_{e1,h1}^{pol}$  are shown as a function of  $\epsilon_{out}$  for a [001] wire of diameter  $D = 3.3$  nm. The direct Coulomb interaction (excluding surface-polarization effect)  $J_{e1,h1}^{dir}$  is shown as a solid (horizontal) line for comparison.

using  $\epsilon_{in} = 11.85$  (Ref. 40) for the Si wire and  $\epsilon_{out} = 1-5$  for the surrounding material. The calculations are performed for the [001] wire with diameter  $D = 3.3$  nm. Figure 7 shows calculated surface-polarization potential  $\Sigma(r)$ . There is a sharp transition from positive to negative value near the wire surface, and the transition smears off with increasing  $\epsilon_{out}$ . These are typical behaviors of surface-polarization potentials, also consistent with analytic expressions.<sup>28,49,50</sup>

The dielectric mismatch mainly contributes two opposite terms to the exciton energies (optical band gap): the self-energy of the electron and the hole, which tends to increase the band gap, and the electron-hole Coulomb interaction, which tends to decrease the band gap. Figure 8 shows the surface-polarization contribution to the self-energy ( $\Sigma_{e1}^{pol} + \Sigma_{h1}^{pol}$ ) and the Coulomb interaction ( $-J_{e1,h1}^{pol}$ ) as a function of  $\epsilon_{out}$ . Both terms are remarkably enhanced for small values of  $\epsilon_{out}$ . The correction from self-energy is significant:  $\Sigma_{e1}^{pol} + \Sigma_{h1}^{pol}$  reaches  $\sim 400$  meV at  $\epsilon_{out} = 1$ , which agrees well with previous tight-binding results.<sup>28</sup> The enhancement of the exciton binding energy is also pronounced, as demonstrated in Refs. 49 and 50, e.g.,  $J_{e1,h1}^{pol} \sim 250$  meV for  $\epsilon_{out} = 1$ , by comparison with  $J_{e1,h1}^{dir} \sim 60$  meV. In three-dimensional quantum dots, it was demonstrated that  $\Sigma_{e1}^{pol} + \Sigma_{h1}^{pol}$  and  $J_{e1,h1}^{pol}$  tend to cancel each other, and thus the surface polarization has a negligible effect on the optical band gap.<sup>43</sup> In Si wires, the cancellation is not complete and the correction to the optical band gap is positive. For other wires, negative (in CdSe)<sup>51</sup> and zero (in PbSe)<sup>52</sup>

corrections were reported. The underlying mechanism is still under investigation and might be related to the different band structures and to the electron-to-hole effective-mass ratio.<sup>52</sup>

Interestingly, we do not observe substantial change of the exchange interaction after including the dielectric mismatch, at least in our perturbative approach. The corresponding value of the exchange splitting,  $K_{e1,h1}^{pol}$ , is less than  $1 \mu\text{eV}$ . This demonstrates that the exchange interaction is predominantly enhanced by spatial confinement, not by dielectric mismatch. However, it should be mentioned that exciton localization near the wire axis induced by enhanced exciton binding ( $J^{pol}$ ) can lead to increased electron-hole exchange interaction. Another consequence of dielectric mismatch is the local-field effect, which leads to a strong suppression of lights polarized perpendicular to the wire axis within the framework of classical electromagnetic theory.<sup>53</sup> The evaluation of these effect is beyond the scope of this work.

## V. SUMMARY

We have presented a detailed study of electronic and excitonic properties on different energy scales for Si nanowires along the [001] and [011] growth direction. In the high-energy single-particle energy scale, we predict an interesting electronic state crossover signaled by the switching of symmetry of the LUMO state with wire diameter for [001]-oriented wires (but not for [011]). This crossover leads to the formation of distinct exciton groups at different diameter regions in [001] wires. The orbitally forbidden low-energy transitions in the medium-diameter region may result in a large Stokes shift, which can be probed experimentally. This result highlights the important role of intervalley coupling in determining electronic and optical properties of indirect band-gap nanomaterials. In the low-energy many-body excitonic energy scale, we describe the excitonic states of Si wires for different sizes and orientation, and provide a systematic analysis of symmetry, polarization, and fine-structure splitting of several excitonic lines. The size dependence of excitonic band gap, exciton binding energy, and exciton lifetime are calculated. The effects of dielectric mismatch on exciton binding energy and exchange splitting are discussed. The current study could be helpful for gaining insight into the electronic and optical properties of Si nanowires toward future optoelectronic applications.

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