

Surface properties of hexagonal Si and Ge: First-principles study of energetics, atomic relaxation, and electronic structure

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Low-index surfaces of hexagonal (lonsdaleite) silicon and germanium polytypes, 2H-Si and 2H-Ge, are investigated using density functional theory calculations for structural optimization and approximate quasiparticle methods for electronic structure analysis. We examine the relaxed geometries of four surface orientations: (1120) *a* plane, (1100) *m* plane, (1102) *r* plane, and (0001) *c* plane, encompassing nine distinct terminations. Our calculations reveal a clear energetic hierarchy with surface excess energies increasing in the order: *m* plane < *a* plane < *r* plane < *c* plane. Surface atomic relaxations are driven by the tendency to eliminate dangling bonds through either pairing or complete filling/emptying with electrons, effectively rendering the surfaces insulating. This behavior is evidenced by the formation of energy gaps between surface-bound states within the fundamental band gap region when projected onto the bulk band structure. We apply approximate quasiparticle methods such as the hybrid functional HSE06 and the shell-LDA-1/2 approach for an accurate description of the band structures. We calculate surface-dependent ionization potentials and electron affinities, and compare our findings with previous results for diamond-structure Si and Ge crystals. These results provide fundamental insights into the surface physics of hexagonal group-IV semiconductors and their potential applications in nanoelectronics.

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I. INTRODUCTION

The group-IV elements silicon (Si) and germanium (Ge) crystallize in the cubic (3C) diamond structure with space group $Fd\bar{3}m$ (O_h^7) under ambient conditions. Thanks to its stable native oxide, the 3C-Si polytype represents the most important semiconducting material for microelectronics and photovoltaics. However, diamond Si and Ge are indirect semiconductors, which limits their application in active optoelectronic devices. Recent years have witnessed significant progress in synthesizing hexagonal lonsdaleite Si and Ge crystals with space group $P6_3/mmc$ (D_{6h}^4), opening new possibilities to exploit the direct—more precisely quasidirect—band gap character of 2H-Ge [1], while 2H-Si remains an indirect material [2]. Hexagonal Ge-rich Si_xGe_{1-x} alloys with enhanced oscillator strengths are predicted to be promising candidates [3–5] for light-emitting device applications.

Various synthesis methods have been developed for hexagonal polytypes of Si, Ge, and Si_xGe_{1-x} . One particularly important approach involves their deposition on wurtzite templates, especially wurtzite III–V nanowires such as 2H-GaAs or 2H-GaP [3,6–13] with {1100} facets. However, especially

for 2H-Si other preparation techniques such as nanoindentation [14] or high-pressure application [15] are common. The resulting core-shell nanowires are characterized by specific facet orientations and high surface area-to-volume ratios of the group-IV overlayers. Consequently, interface properties, surface orientation, and total energy play crucial roles in determining local growth patterns, lateral morphology, and stability as functions of both the III–V semiconductor core diameter [16,17] and the hexagonal Si and Ge shell thickness [18,19].

Surface energies [20,21] fundamentally determine the morphology of nanowires [19] and nanocrystals [22]. According to the Wulff theorem [23–25], equilibrium crystal shapes are determined by minimizing the total surface excess free energy, resulting in structures such as tetrakaidecahedrons with (111), (110), (311), and (100) facets [22]. Surface energies are important not only for material-vacuum interfaces but also for heterointerface formation, such as between hexagonal Ge and Si_xGe_{1-x} [26]. Understanding surface stability is particularly crucial for supporting experimental efforts to achieve epitaxial growth of hexagonal thin-films of Si and Ge. These excess surface energies depend on the total energies of both the surface-containing semiconducting system and the corresponding bulk material, and are therefore influenced by surface geometry and electronic band structure energies [24].

For cubic Si and Ge, experimental surface energy values are known to range from 1.1–1.9 J/m² and 1.0–1.7 J/m², respectively [27,28]. More recent measurements report smaller values of 1.2–1.4 J/m² for Si [25,29], with orientation-dependent variations in good agreement with

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ab initio calculations. Theoretical values range from 1.3–1.7 J/m² [18,20,21] for reconstructed Si surfaces to 1.45–1.85 J/m² [19–21] for relaxed surfaces. Reconstructed Ge surfaces exhibit smaller surface energies of 0.92–1.17 J/m² [18,20,21]. These values also depend on the exchange-correlation (XC) functionals employed in DFT calculations [30], with the local density approximation (LDA) [31] typically yielding higher energies than the generalized gradient approximation (GGA) [32]. Recently, the first attempts to compute surface excess energies for hexagonal lonsdaleite Si and Ge surfaces have been published [18,19], indicating slightly smaller energies compared to their cubic counterparts.

While the geometries and band structures of relaxed or reconstructed low-index surfaces of diamond-structure Si and Ge crystals have been extensively investigated and are well understood (see Ref. [24] for an overview), the surfaces of hexagonal Si and Ge crystals remain largely unexplored both theoretically and experimentally. Beyond surface energetics, detailed knowledge of their atomic geometry and surface band structures is currently lacking.

In this work, we present a comprehensive investigation of the (11 $\bar{2}$ 0) *a*-plane, (1 $\bar{1}$ 00) *m*-plane, (1 $\bar{1}$ 02) *r*-plane, and (0001) *c*-plane surfaces of lonsdaleite Si and Ge crystals using DFT for structural and energetic properties and approximate quasiparticle approaches for electronic structure analysis. We focus on relaxed surfaces with 1 $\times$ 1 unit cells to investigate the potential (in)stability of Si and Ge interfaces with substrates for two-dimensional growth, as well as the fundamental properties of cleaved or differently prepared surfaces. The study of reconstructed surfaces with larger unit cells, while important, represents a separate and extensive research program that warrants dedicated future investigation. The computational methods are described in Sec. II, including discussion of the challenges associated with modeling surfaces of various orientations using the slab method. Section III presents results for relaxed surfaces with different orientations, examining atomic relaxation relative to bulk positions and discussing the thermodynamic stability of hexagonal crystal surfaces based on computed surface energies. We analyze the relationship between surface band structures, dangling bond density per surface unit cell, and specific atomic displacements. From the electronic structures and their alignment, we derive bulk and surface ionization potentials and electron affinities. Finally, Sec. IV provides a summary and conclusions.

II. NUMERICAL AND THEORETICAL APPROACHES

A. Structure and energy

All ground-state DFT calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP) [33,34]. Wave functions and pseudopotentials were described within the projector-augmented wave method [35], with shallow Ge 3*d* electrons treated as valence electrons. Spin-orbit coupling (SOC) was included in electronic structure calculations but not in geometry optimizations due to its negligible influence on atomic positions. The plane-wave expansion employs kinetic-energy cutoffs of 300 eV for Si and 500 eV for Ge systems.

Exchange and correlation effects were treated using the PBEsol functional [36], which is derived within the GGA framework. Brillouin-zone (BZ) integrations were performed using Γ -centered Monkhorst-Pack meshes [37], with grid densities adapted according to the dimensions of the three-dimensional (3D) slabs. For bulk lonsdaleite calculations, we employed 12 $\times$ 12 $\times$ 6 *k*-point meshes within the 3D-BZ of the hexagonal unit cell containing four atoms. For slab calculations, the mesh density was inversely scaled with the lattice vector lengths to maintain consistent sampling quality across different system sizes.

B. Band structure description

To compute approximate quasiparticle (QP) band structures that account for excitation effects beyond the Kohn-Sham (KS) bands of DFT [31], we investigate three computational approaches that are known to yield reliable band structures with a contained computational effort. These methods are illustrated in Fig. 1 for bulk lonsdaleite 2H-Ge and 2H-Si. Full quasiparticle calculations within Hedin's GW approximation [38] are computationally prohibitive for our systems, which contain slabs with $\sim$ 50 atoms and 14 *s*, *p*, and *d* electrons per Ge atom.

The first approximate method employs a meta-GGA exchange-correlation functional based on the modified Becke-Johnson (MBJ) exchange potential [39]. This MBJ exchange functional [40,41], typically combined with DFT-LDA, yields fundamental energy gaps for hexagonal and cubic polytypes of Si and Ge in excellent agreement with experimental data and advanced many-body descriptions (see Refs. [2,42] and references therein). Although the MBJLDA method was originally developed for macroscopic homogeneous bulk crystals, generalizations to inhomogeneous systems with surfaces between bulk regions and vacuum are available [43,44]. Here, we employ a bulk-like approximation where the parameter *c* of the MBJ exchange potential is set to the bulk values: *c* = 1.13 for 2H-Si and *c* = 1.21 for 2H-Ge, despite slight dependence on vacuum region extent. This approach follows the common practice of applying identical exchange-correlation functionals and atomic pseudopotentials in both bulk and surface calculations, whose validity has been demonstrated for diamond-structure surfaces such as Ge(001)4 $\times$ 2 [45] and Si(111)2 $\times$ 1 [46].

The second method utilizes a hybrid functional with nonlocal screened exchange interaction according to Heyd, Scuseria, and Ernzerhof [47,48]. This HSE06 approach also provides reliable energy gaps for bulk Si and Ge polytypes, regardless of their cubic or hexagonal symmetry [1,2,42]. The direct and indirect gaps of diamond- and lonsdaleite-Si and Ge polytypes calculated with HSE06 show excellent mutual agreement and consistency with available experimental data. Both MBJLDA and HSE06 have been successfully applied for describing band lineups at heterointerfaces between hexagonal SiGe alloys with different compositions [49,50] and for modeling quantum well structures [26].

The third approximate QP method is the LDA-1/2 approach [51,52], which has proven effective for describing electronic structures of hexagonal compound surfaces [53]. In particular, its improved version, the shell-LDA-1/2 method

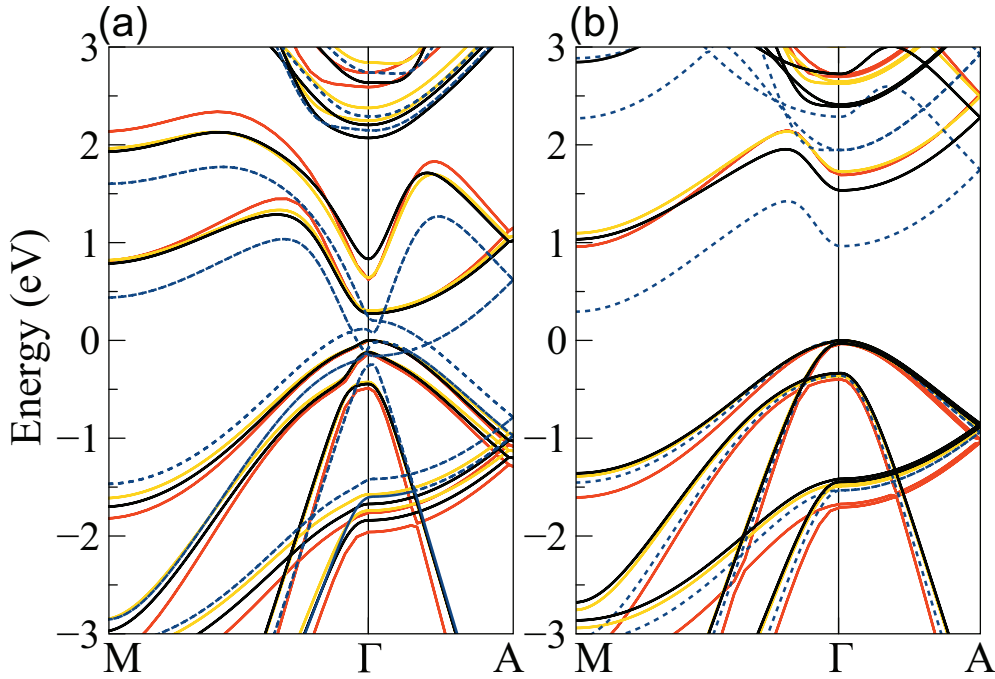


FIG. 1. Band structures of (a) 2H-Ge (b) 2H-Si calculated in the framework of three approximations to account for the QP excitation aspect: MBJLDA (yellow solid lines), HSE06 (red solid lines), LDA-1/2 (black solid lines), and PBEsol (blue dotted lines) in an area around the fundamental gap at the Γ point. The valence band maximum is chosen as energy zero.

[54], delivers excellent band gaps for group-IV materials. Figure 1(a) demonstrates that all three approximate methods—MBJLDA, HSE06, and shell-LDA-1/2—yield consistent results for the lowest conduction and highest valence bands of 2H-Ge, including both energy positions relative to the valence band maximum (VBM, used as energy zero) and band dispersions. The direct gap values are 0.30 eV (MBJLDA), 0.29 eV (HSE06), and 0.28 eV (LDA-1/2), confirming that all methods are suitable for studying surface state bands within the fundamental gap region. The most important effect of the considered approximate quasiparticle methods is to open the band gap that is absent in PBEsol calculations. The gap opening and the resulting similar quasiparticle bands are also visible in the band structures of 2H-Si in Fig. 1(b). The indirect gap increases from 0.29 eV (PBEsol) to 0.98 eV (HSE06), 1.03 eV (LDA-1/2), or 1.10 eV (MBJLDA). For the direct gaps, these values are 0.96 eV (PBEsol), 1.69 eV (HSE06), 1.80 eV (LDA-1/2), and 1.73 eV (MBJLDA).

For practical implementation, we apply the HSE06 method to Si slab band structures, while the computational demands render this approach prohibitive for Ge slabs. In fact, the number of valence electrons increases from 4 to 14 when going from Si to Ge, and the presence of semicore states requires increasing the plane-wave cutoff from 300 to 500 eV. The MBJLDA method exhibits convergence difficulties for large vacuum regions, unlike the case of interface calculations [26]. Consequently, we employ the shell-LDA-1/2 method for all Ge slab systems.

To identify surface bound and resonance states, the resulting slab band structures in the two-dimensional (2D) Brillouin zone of the studied surfaces must be aligned with bulk

band structures projected onto the corresponding 2D-BZ. We perform this alignment using electrostatic potentials averaged over planes perpendicular to the surface normal, evaluated at the center of the slab for both the slab system and the corresponding bulk [55]. For the [0001] case, this alignment procedure has been validated to yield results similar to those obtained using branch-point energy alignment [49].

C. Surface modeling

We employ the repeated slab method [24] to model the surfaces of interest. Starting from a 3D lonsdaleite crystal with lattice constants a and c and Bravais lattice vectors $\mathbf{a}_1 = a(1, 0, 0)$, $\mathbf{a}_2 = \frac{a}{2}(-1, \sqrt{3}, 0)$, and $\mathbf{a}_3 = c(0, 0, 1)$, we remove atoms to create vacuum regions with thickness of at least 20 Å and material layers arranged periodically perpendicular to the surface. These material layers possess two-dimensional translational symmetry.

The resulting slabs are constrained to have symmetric top and bottom surfaces. Their 2D unit cells perpendicular to the surface normal are formed by primitive basis vectors $\mathbf{a}$ and $\mathbf{b}$, which span the plane with Miller indices (hki) where $h + k + i = 0$. We construct $\mathbf{a}$ and $\mathbf{b}$ from the crystal Bravais vectors through orthogonal transformation. For the 3D slab arrangement, an additional basis vector $\mathbf{c}$ must be introduced. We focus on the smallest 2D 1×1 unit cells for each surface orientation $\mathbf{n}$ to maintain computational cost contained, while recognizing that restricting to 1×1 translational symmetry may miss important surface reconstructions that could further lower surface energies. Table I presents the chosen lattice vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}/N$ (where N represents the number of atomic layers) for describing the $(1\bar{1}00)$, $(11\bar{2}0)$, $(1\bar{1}02)$, and (0001) surfaces, along with their corresponding surface normals.

TABLE I. Lattice vectors of the smallest unit cells in the considered surfaces and corresponding surface normals.

Facet	$\mathbf{a}$	$\mathbf{b}$	$\mathbf{c}/N$	$\mathbf{n}$
a	$\mathbf{a}_3$	$\mathbf{a}_2 - \mathbf{a}_1$	$-\mathbf{a}_1$	$\frac{1}{\sqrt{12}}(-3, -\sqrt{3}, 0)$
m	$\mathbf{a}_3$	$\mathbf{a}_1 + \mathbf{a}_2$	$\mathbf{a}_2$	$(-\frac{\sqrt{3}}{2}, \frac{1}{2}, 0)$
c	$\mathbf{a}_1$	$\mathbf{a}_2$	$\mathbf{a}_3$	$(0, 0, 1)$
r	$\mathbf{a}_1 + \mathbf{a}_2$	$\mathbf{a}_2 - \mathbf{a}_1 + \mathbf{a}_3$	$\mathbf{a}_3$	$\frac{1}{2\sqrt{\frac{c^2}{a^2} + \frac{3}{4}}}(\sqrt{3}\frac{c}{a}, -\frac{c}{a}, -\sqrt{3})$

The third vector $\mathbf{c}$ is oriented out of the $(hkil)$ plane but is not necessarily parallel to the surface normal $\mathbf{n}$. Following standard practice, we choose the “most orthogonal” vector $\mathbf{c}$ to enable fine control of the cell size [24,25,56]. Figure 2 illustrates the slabs used for a , m , and r surfaces (with oblique vector $\mathbf{c}$) as well as the slabs for c surfaces (with orthogonal $\mathbf{c}$).

The surface termination—that is, the atomic structure of the surface—plays a crucial role in determining surface properties. Figure 2 shows that different termination variants exist: four different variants appear for the r -plane case, two variants for the m plane, and one variant for the a -plane surfaces. For c -plane surfaces, we observe either single-dangling bond (SDB) or triple-dangling bond (TDB) terminations. In the cases of a , m , and r planes, multiple atoms exist within the surface unit cell, enabling dangling bond pairing similar to that observed in reconstructed surfaces of cubic polytypes [20,24]. For

c -plane surfaces, SOC inclusion allows for exchange-driven level splitting and the formation of magnetic surfaces.

The slabs shown in Fig. 2 must be sufficiently thick to ensure converged results for surface energies, geometries, and band structures. The lattice vector $\mathbf{c}$ should be reasonably orthogonal to $\mathbf{a}$ and $\mathbf{b}$ [56] to guarantee that dispersion effects in the 2D $\mathbf{k}$ -space parallel to the surface plane are negligible. For c -plane (0001) surfaces, $\mathbf{c}$ is parallel to $\mathbf{n}$, resulting in hexagonal slabs. To achieve convergence of the surface energy, we varied the number of atomic layers in test calculations. The results are similar to findings for cubic Si and Ge crystals [20,57]. We employ 14 atomic layers for a -plane surfaces, 18 or 20 layers for m -plane surfaces, 42, 44, or 46 layers for r -plane surfaces, and 16 or 18 layers for c -plane surfaces within the monoclinic description. See Table V in the Appendix V for convergence with the number of layers at the example of the c plane. Test calculations for m surfaces with 20 atomic layers demonstrate that surface energies vary by no more than the magnitude of numerical errors when comparing monoclinic and orthorhombic slab geometries.

D. Surface energy

We relax the atomic geometries in both surface regions of the slab (see Fig. 3) until the Hellmann-Feynman forces fall below 10 meV/Å. The resulting energy values become less sensitive to the total number of layers when at least 18 layers are used. Previous studies have demonstrated that relaxing four to six layers on both slab sides is sufficient for convergence [20,24,58]. We relax four layers for the a - and c -plane orientations and the equivalent height of four double

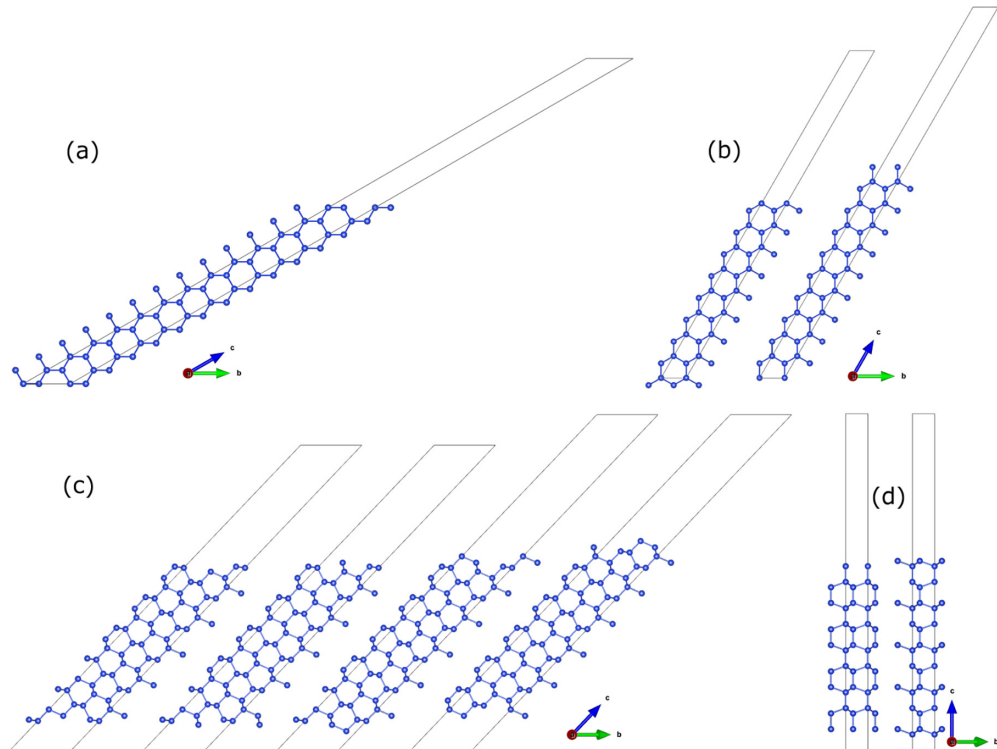


FIG. 2. Symmetric monoclinic or hexagonal slabs used for modeling of (a) a -plane ($11\bar{2}0$), (b) m -plane ($1\bar{1}00$), (c) r -plane ($10\bar{1}2$), and (d) c -plane surfaces with variations of the surface geometries 1 (a), 2 (b), 4 (c), and 2 (d), respectively.

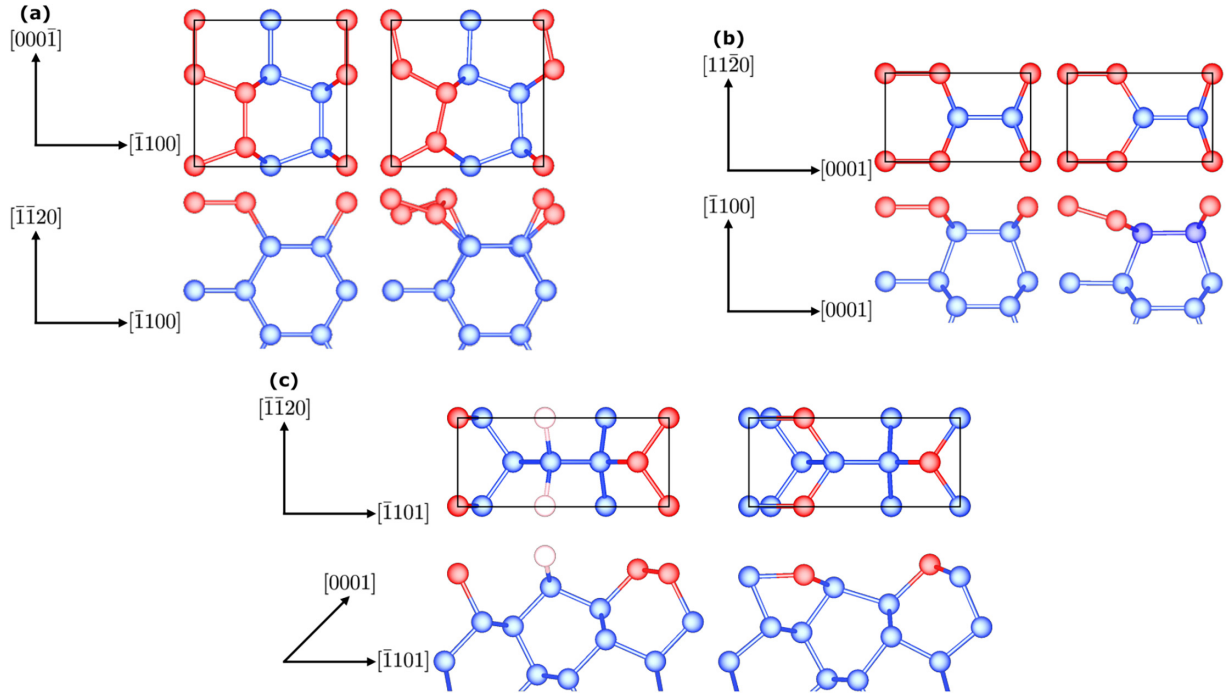


FIG. 3. Top (upper panel) and side (lower panel) view of the lowest-energy (a) $(11\bar{2}0)$ a plane, (b) $(1\bar{1}00)$ m plane, and (c) $(1\bar{1}02)$ r plane. Left (right) panels represent the unrelaxed (relaxed) surface geometry. Only a few atomic layers are presented. Surface atoms with one (two) DBs are illustrated by red (pink) color. The atoms in layers beneath the surface are represented by blue circles. The surface unit cells are marked by black rectangles.

layers for the r plane. For the m -plane case, we relax all atoms due to the high sensitivity of its electronic structure to small changes in atomic coordinates.

Using the total energy per atom E_{bulk} of the bulk system computed within the same slab approximation but without a vacuum region, we calculate the surface (excess) energy as

$$\gamma = \frac{1}{2A} [E_{\text{slab}}(N) - N \times E_{\text{bulk}}], \quad (1)$$

where A denotes the area of the 2D surface unit cell. Similar calculations are commonly performed for two-dimensional defects such as stacking faults [59].

III. RESULTS AND DISCUSSION

A. Surface geometry and atomic relaxation

The $(1\bar{1}00)$ m -plane surface contains four atoms in the surface unit cell [see Fig. 3(a)] distributed across two atomic layers, where the uppermost two atoms possess either one (termination 1) or two (termination 2) dangling bonds (DBs) (see Table II). Consequently, termination 1 is energetically favored over termination 2 by approximately a factor of two for unrelaxed bulk-derived geometries.

The atomic relaxation, which preserves the 1×1 translational symmetry, is dominated by the interaction between two DBs of adjacent surface atoms connected by an in-plane bond via two sp^3 hybrids. Two relaxation mechanisms are possible: (i) a buckling mechanism leading to a puckered surface, or (ii) dimerization between adjacent atoms connected by an in-plane bond. In mechanism (i), one atom moves out of the surface, creating a filled, more s -like dangling

bond and three more p -like orbitals in the backbonds. The second atom, displaced toward the bulk, forms an empty, more p -like orbital and sp^2 -like orbitals in bonds to its three neighbors. The energy gain (see Table II) compared to the ideal surface results primarily from electron transfer from a group-IV p orbital to a corresponding neighboring s orbital. Such buckling/puckering mechanisms with lone pair formation in s -like surface states to lower surface energy have been observed in surface reconstructions of 3C-Si crystals [58], particularly for (112) or (110) surface reconstructions [60,61]. In the dimerized case (ii), two adjacent atoms form sp^3 bonds in the $[0001]$ direction, leading to pairing and downward movement of these atoms, forming a σ bond between two sp -like orbitals pointing toward each other in the surface plane and a π bond between two parallel p -like orbitals parallel to the surface normal [24]. The resulting double bond should lower the surface energy. Total energy minimization favors the buckling mechanism, as clearly shown in the right, lower panel of Fig. 3(b). The two surface atoms in the second atomic layer with four nearest neighbors are less affected by relaxation (see Table III).

The consequences of the buckling mechanism at the m -plane surfaces are illustrated in Figs. 4(c) and 4(d). The squared wave functions of the surface band states at the $\bar{M}$ point in the BZ are plotted for both the empty surface state and the occupied surface band. The subfigures clearly show the different behavior for the outward and inward buckled surface atoms.

One of the threefold-coordinated atoms in the surface unit cell with area $A_m = ac$ is displaced by 0.54 (0.52) Å for Ge (Si) toward the bulk, forming sp^2 hybrids in bonds to its three

TABLE II. Surface energies γ in meV/Å² (in J/m² in parenthesis) for unrelaxed and relaxed a , m , r , and c surfaces of 2H-Si and -Ge with different terminations characterized by the number n_A of surface atoms and n_{DB} dangling bonds in a surface unit cell. The DB density ρ_{DB} is also given in units of 10⁻² Å⁻². Energies from other calculations [18,19] are also listed in the last two columns for Si and Ge each.

Surface	Termination	n_A	n_{DB}	ρ_{DB} Si/Ge	Surface energy							
					Si				Ge			
					Unrelaxed		Relaxed		Unrelaxed		Relaxed	
a (11 $\bar{2}$ 0)	1	8	4	9.54/8.78	100.1 (1.60)	85.8 (1.37)	79.1	91	75.7 (1.21)	59.8 (0.96)	50.1	66
m (1 $\bar{1}$ 00)	1	4	2	8.26/7.60	91.1 (1.46)	78.6 (1.26)	72.6	105	68.0 (1.09)	55.7 (0.89)	47.6	75
	2	4	4	16.52/15.20	160.3 (2.57)	159.2 (2.55)			112.9 (1.81)	112.2 (1.80)		
c (0001)	1	1	1	7.89/7.24	106.5 (1.71)	105.0 (1.68)	78.6	99	79.2 (1.27)	78.9 (1.26)		74
	2	1	3	23.66/21.73	183.9 (2.95)	183.7 (2.94)			127.0 (2.03)	126.1 (2.02)		
r (1 $\bar{1}$ 02)	1	4	4	11.41/10.49	130.8 (2.10)	115.7 (1.85)			94.4 (1.51)	76.6 (1.23)		
	2	4	4	5.70/5.24	131.0 (2.10)	96.7 (1.55)			93.6 (1.50)	70.1 (1.12)		
	3	4	4	14.11/10.49	131.1 (2.10)	115.0 (1.84)			94.5 (1.51)	80.2 (1.28)		
	4	4	4	14.11/10.49	131.1 (2.10)	115.0 (1.84)			94.5 (1.51)	80.2 (1.28)		

neighbors and a p_z -like orbital pointing along the surface normal that becomes unoccupied. The second uppermost surface atom is displaced outward by 0.28 (0.13) Å, with a tendency toward p -like orbitals to the neighbors and a more s -like DB that is filled with two electrons to gain energy.

The (11 $\bar{2}$ 0) 1×1 a -plane surface has a larger 2D unit cell with area $A_a = \sqrt{3}ac$ compared to the (1 $\bar{1}$ 00) 1×1 m -plane case. Consequently, the number of atoms in the two surface atomic layers [see Fig. 3(a)] increases from four to eight,

with half showing one DB. Despite the smaller DB density (cf. Table II), the flexibility of possible atomic displacements increases during surface relaxation. Again, the possible mechanisms are pairwise correlated rearrangements via buckling or dimerization. These are arranged in zigzag chains with atoms at nearest-neighbor distances parallel to the c axis of the bulk 2H crystal. The chain with fourfold-coordinated atoms is situated in the second atomic layer, 1.99 (1.92) Å below the first layer for Ge (Si). The atoms with one DB in the upper

TABLE III. Atomic displacements of surface atoms along the $\mathbf{a}$ (x), $\mathbf{b}$ (y) edges and the surface normal $\mathbf{n}$ (z) (in Å) listed for the lowest-energy arrangement of the a , m , c , and r surfaces of 2H-Ge and 2H-Si.

Surface	Atomic layer	Displacements (in Å) in Cartesian directions					
		Ge			Si		
		x	y	z	x	y	z
a	First	-0.23	0.37	-0.50	-0.21	0.36	-0.50
	First	-0.01	-0.13	0.25	0.02	-0.10	0.14
	First	-0.01	0.13	0.25	0.02	0.10	0.14
	First	-0.23	-0.37	-0.50	-0.21	-0.36	-0.50
	Second	0.02	-0.07	0.07	0.02	-0.05	0.05
	Second	0.03	0.05	0.01	0.04	0.05	0.00
	Second	0.03	-0.05	0.01	0.04	-0.05	0.00
	Second	0.02	0.07	0.07	0.02	0.05	0.05
m	First	0.11	0.00	0.28	-0.30	0.00	-0.52
	First	0.33	0.00	-0.54	-0.08	0.00	0.13
	Second	-0.12	0.00	0.08	0.07	0.00	0.02
	Second	-0.11	0.00	0.05	0.07	0.00	0.04
c	First	0.00	0.00	0.04	0.00	0.00	-0.05
	Second	0.00	0.00	0.02	0.00	0.00	0.03
r	First	0.00	-1.21	-0.67	0.00	-1.23	-0.78
	Second	0.00	0.21	0.48	0.00	0.21	0.27
	Third	0.00	0.16	-0.08	0.00	0.17	-0.08
	Fourth	0.00	-0.11	0.08	0.00	-0.17	0.03
	Fifth	0.00	0.15	0.28	0.00	0.08	0.23
	Sixth	0.00	-0.01	-0.16	0.00	0.03	-0.17
	Seventh	0.00	0.03	-0.14	0.00	0.03	-0.19
	Eighth	0.00	-0.08	0.17	0.00	-0.06	0.16
	Ninth	0.00	-0.13	-0.01	0.00	-0.11	0.00

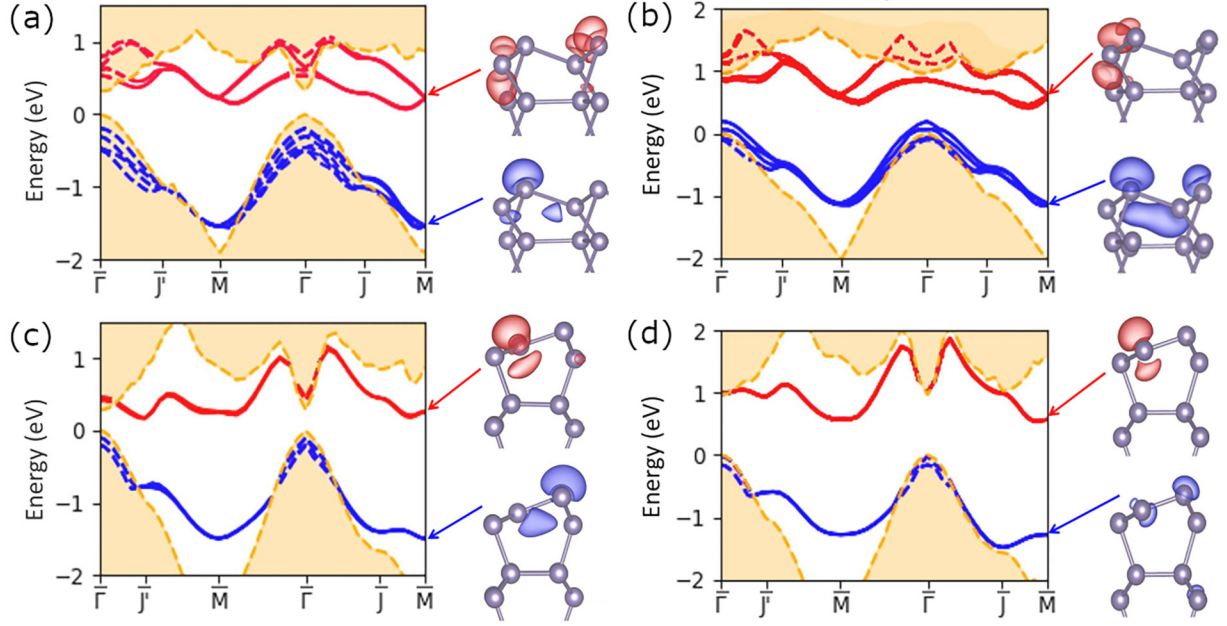


FIG. 4. Lowest-energy empty (red) and highest-energy occupied (blue) surface states at the $\bar{M}$ point of the surface BZ for (a), (b) a -plane and (c), (d) m -plane surfaces of (a), (c) 2H-Ge and (b), (d) 2H-Si. The wave-function squares are depicted together with the surface geometries (side view).

chain exhibit the strongest displacements after relaxation. Two atoms with one DB at equivalent positions along the $[\bar{1}100]$ axis in the chain form a pair whose atoms behave similarly during relaxation (see Table III). The two pairs relax while conserving symmetry across a plane containing the $[1\bar{1}00]$ axis and a normal in the $[0001]$ direction [see Fig. 3(a) and Table III]. The two pairs rotate by $12 - 13^\circ$ against the c axis. These twists are accompanied by equal buckling movements of -0.50 (-0.50) Å and 0.25 (0.14) Å for the two atoms in each pair for Ge (Si). The two pair atoms moving toward the bulk form flat sp^2 orbitals in bonds to their three neighbors. The outward-moving atom forms three bonds to its neighbors with p -like orbitals. Its resulting s -like DB captures the electron from the p_z -like DB of the neighboring atom in the pair and forms a lone pair, providing significant energy gain on the order of the difference between s - and p -orbital energies of the two elements. The buckling of pairs in the chain with accompanying strong hybridization can be summarized as surface puckering [58], where strong geometric modifications in the first layer still yield effective energy gain.

The consequences of the surface relaxation for the dangling bonds and backbonds in the a plane cases are illustrated in Figs. 4(a) and 4(b). More precisely, the wave functions of the surface states at the $\bar{M}$ point with the complete degeneracy of the empty and occupied surface bands are plotted. The probabilities of finding an electron or a hole in such surface states have been mentioned above. In the a -plane case, the location of the occupied surface state is more extended for Si as a consequence of the energetic equivalence of occupied surface bands with the projected bulk valence band structure.

The $(1\bar{1}02)1 \times 1$ r -surfaces, which are tilted with respect to the c axis, also possess rectangular 2D unit cells with edge lengths a and $\sqrt{3a^2 + c^2}$ and contain two atoms with one DB and one atom with two DBs

[see Fig. 3(c) and Table II]. The dangling bond density amounts to $4/A_r = 0.1141$ (0.1049) Å $^{-2}$ with a unit cell area of $A_r = 35.055$ (38.142) Å ^{2} for 2H-Si (Ge), which is larger than that of the a plane with four DBs and the m plane with only two DBs per unit cell. We identified four different surface terminations, all of which have higher surface energies than the a - and m -plane surfaces. Therefore, we discuss only the relaxed geometry and electronic structure of the lowest total energy termination in detail.

The most reactive surface atom with two DBs is significantly displaced toward the bulk and simultaneously toward another surface atom in the second-nearest-neighbor position to form a fivefold ring, well known from surface reconstructions [21,62]. Another surface atom with one DB moves toward this atom, forming a chemical bond [see Fig. 3(c)] and passivating two DBs. Due to its three resulting sp^3 hybrids, the surface atom with originally two DBs forms a remaining p_z -DB that becomes empty. Its electron fills the DB of the remaining surface atom, forming a lone pair.

The $(0001)1 \times 1$ c -plane surface [Fig. 2(d)] with one atom per unit cell with area $A_c = 12.679$ (13.808) Å ^{2} for Si (Ge) contains either one or three DBs, leading to surfaces with the lowest or highest DB density, respectively. We focus on the single-DB surface, the $c1$ configuration. Its relaxation behavior closely resembles that of the $(111)1 \times 1$ surface of the diamond structure [20], which shows slight inward relaxation to form a compressed silicene or germanene overlayer [62]. Pairing of DBs is not possible while maintaining 1×1 translational symmetry. Only a 2×1 surface reconstruction may transform the metallic surface into an insulating one, combined with very low surface energy and significant rearrangement involving the formation of five-member and seven-member rings of atoms in the two uppermost atomic layers. The tilted Pandey π -bonded chain model [63]

with two isomers [64–66] appears to describe the 2×1 reconstruction.

The inclusion of SOC leads to magnetic surface properties. A ferromagnetic arrangement of surface spins significantly lowers the total system energy via exchange energy for both Si and Ge, leading to an insulating ground state at least for Si in the HSE06 framework. For Ge, this trend is weakened due to the small bulk gap. The paramagnetic surface is energetically unfavorable, and an antiferromagnetic surface spin system is impossible due to restrictions of the 1×1 system [64,67].

B. Excess energies

The calculated surface excess energies listed in Table II allow several clear statements regarding trends with surface orientation, surface termination, and group-IV element. The excess energies γ (1) for the most important terminations are approximately 20–30% larger for Si compared to Ge. This finding is in rough agreement with results for diamond structure surfaces [20]. This energy difference due to chemistry also correlates with the experimental cohesive energies of 4.63 (3.85) eV/atom for bulk 3C-Si (3C-Ge) [68]. The lowest-energy surface termination is primarily related to the number of DBs (see m - and c -plane surfaces). For cases with equal numbers, such as the r -plane terminations, the mutual interaction of DBs plays an important role. The influence of the specific group-IV element (Si or Ge) on the energetic favorability of a termination is minimal.

Atomic relaxation at surfaces significantly lowers the surface excess energy by approximately 20% compared to unrelaxed surface values (see Table II). This relaxation effect is more pronounced than for diamond-Si and -Ge surfaces. The reason relates to the larger 1×1 a - and m -surface unit cells of 2H, which already permit atomic displacements that occur only upon surface reconstruction in the diamond case, e.g., for the 2×1 reconstruction [20]. This effect explains why surface energies for a and m planes are lower compared to the nonreconstructed c -plane value. For cubic crystals, the stacking direction (111) is favored over surface orientations (110) and (001) [20].

The absolute surface energies with an upper limit of 1.46 (1.09) J/m² for the favorable ($\bar{1}\bar{1}00$) plane of Si (Ge) without atomic relaxation appear smaller than corresponding theoretical and experimental values for diamond structures [20,21,25]. However, the exchange-correlation functional used and surface reconstruction present during measurements may influence these values. Our PBEsol results for the most stable terminations agree well with PBE results [18] for relaxed a -, m -, and c -plane surfaces of both lonsdaleite crystals, 2H-Si and 2H-Ge. This agreement holds for both absolute values and the energetic sequence: m plane, a plane, and c plane (at least for 1×1 cells and favorable terminations). Only the sequence of a - and c -plane surfaces is not entirely clear because the energies reported by Scalise *et al.* [18] are close to each other. However, the energetic sequence disagrees with DFT treatments applying the LDA [19] to the exchange-correlation functional. This disagreement particularly applies to the finding of relaxed a -plane surfaces of Si and Ge as the energetically most favorable ones. The increase in absolute γ values in LDA compared to PBEsol and PBE may

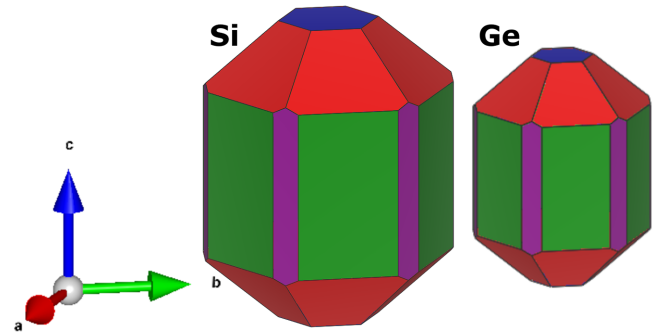


FIG. 5. Wulff construction of hexagonal Si and Ge nanocrystals. The green, purple, red, and blue surfaces are the m -, a -, r -, and c planes, respectively.

relate to the overbinding tendency in LDA compared to the underbinding tendency, especially when applying the PBE exchange-correlation functional.

Our sequence of surface excess energies $\gamma_m < \gamma_a < \gamma_r < \gamma_c$ for relaxed geometries of the lowest-energy terminations enables Wulff construction by minimizing the excess free energy of nanocrystallite surfaces with m -, a -, c -, and r -plane facets with respect to total surface area [24], similar to the diamond case [22]. This construction is shown in Fig. 5. From this analysis, we predict that 2H-Si and 2H-Ge nanowires grown in the c -axis direction will have an almost hexagonal shape consisting of m faces, with small regions of a -faces on the edges. Experimentally, a hexagonal shape composed only of m facets [3,6,7,11,26] has been observed for nanowires (or core-shell nanowires) with diameters (or shell thicknesses) around 100 nm. This discrepancy can be explained by the neglect of edge energies and strain induced by the substrate or core in core-shell nanowires.

C. Surface bands

We present the band structures of Si and Ge slabs in Figs. 6 and 7, respectively, based on the PBEsol-optimized atomic geometries, but using different exchange-correlation approximations to demonstrate the influence of approximately treated QP effects. We employ the PBEsol functional to present Kohn-Sham band structures from DFT for unrelaxed (left panels) and relaxed (middle panels) 1×1 surfaces, demonstrating the direct influence of geometric relaxation on surface electronic states. We study the effect of QP shifts—the excitation aspect—on electronic bands in the right panels. The HSE06 approach is applied only to Si surfaces because the additional 10 d electrons in Ge significantly increase computational load. Instead, we use shell-LDA-1/2 to describe the electronic structure of Ge surfaces. We calculate both types of band structures for relaxed 1×1 surface geometries. We study the surface orientations ($\bar{1}\bar{1}00$), ($1\bar{1}20$), (0001), and ($\bar{1}\bar{1}02$) to illustrate orientation effects. We present only bands for surface geometries that yield minimum total energy with respect to their termination and atomic relaxation while preserving 1×1 translational symmetry. To identify surface bound states in the gap region and surface resonance states that energetically overlap with bulk band states, we present slab band structures together with bulk band

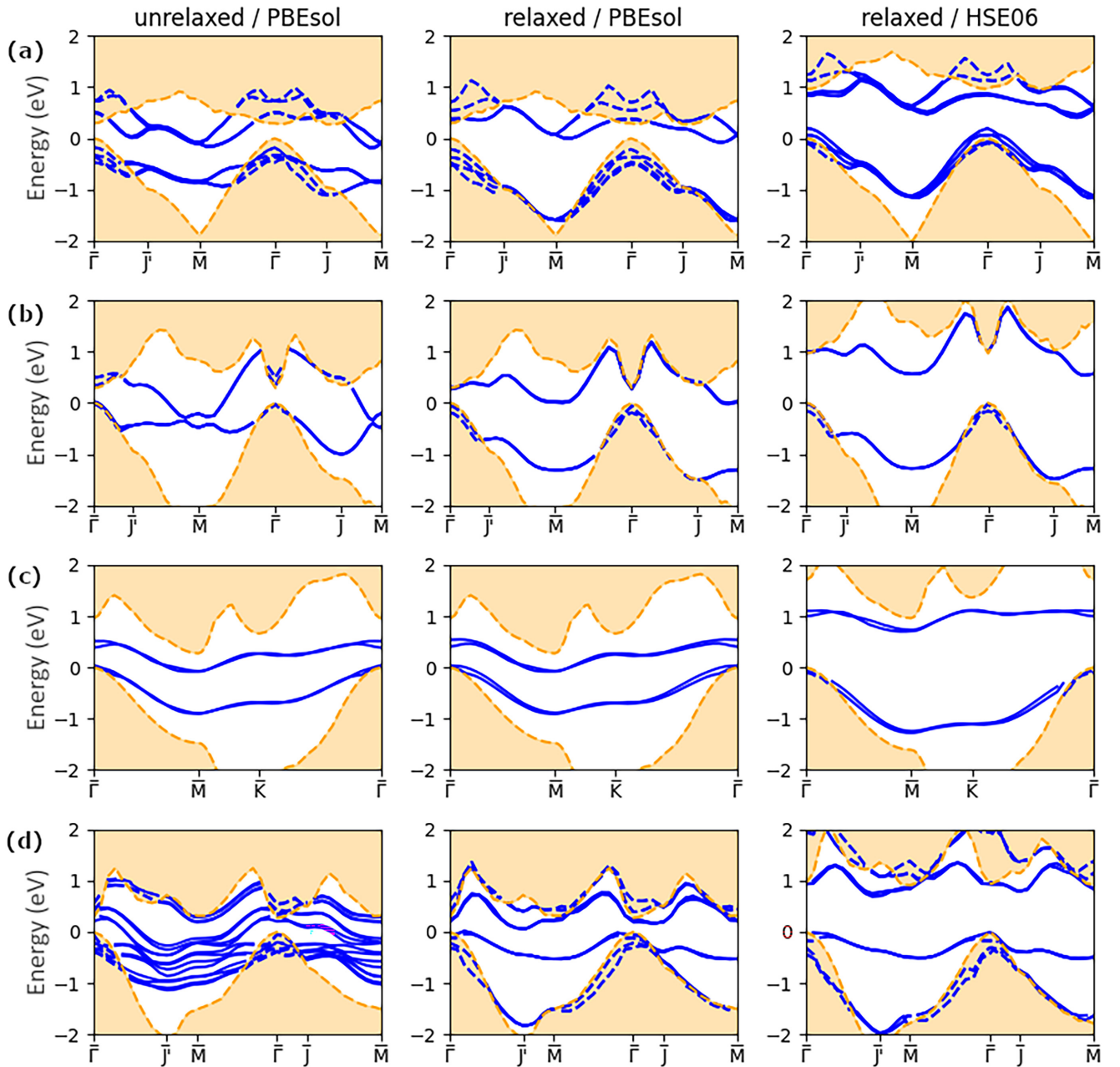


FIG. 6. Slab (blue) and projected bulk (orange) band structures of 2H-Si from DFT obtained with the PBEsol XC potential (left panels) and the approximate QP description in HSE06 versus the 2D surface BZ. The lowest-energy terminations of four different surface orientations are displayed (a) a plane, (b) m plane, (c) c plane, and (d) r plane. The left (middle, right) panel displays the PBEsol (PBEsol, HSE06) band structure for the unrelaxed (relaxed, relaxed) geometry. The 1×1 translational symmetry is kept for all surfaces. Surface bound states in the fundamental gap are displayed by blue solid lines, surface resonance states emerging from the gap into the projected bulk band regions are indicated by blue dashed lines.

structures projected onto the 2D Brillouin zone of the corresponding surface. We align the two (slab and projected bulk) band structures using averaged electrostatic potentials of slab and bulk according to the procedure described in Ref. [55] and illustrated in Fig. 8.

The surface electronic band structures of the considered surfaces with lowest-energy terminations in Figs. 6 and 7 show that for a given orientation, the principal features are largely independent of the group-IV element and the

approximate inclusion or exclusion of QP corrections to band energies. However, surface relaxation and magnetization are important. The dispersion of the lowest conduction band edge and highest valence band edge is determined by surface orientation. The projected bulk valence band top reaches a maximum at Γ and shows a pronounced region without bulk states for high-symmetry lines along Brillouin zone edges. This picture is less clear for 2H-Ge surfaces when the electronic structure is described only by Kohn-Sham bands using

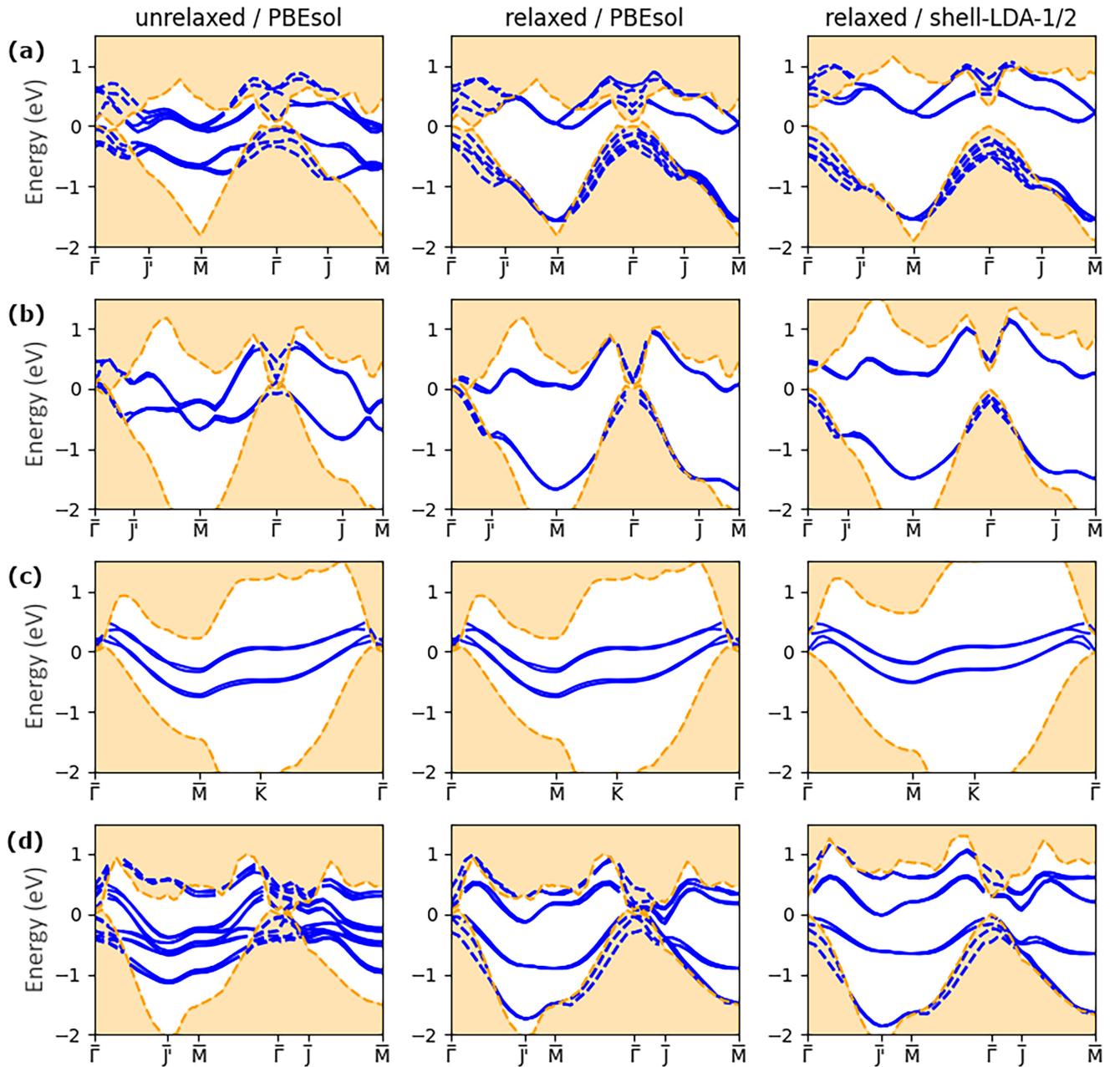


FIG. 7. Slab (blue) and projected bulk (orange) band structures of 2H-Ge from DFT obtained with the PBEsol XC potential (left panels) and the approximate QP description in shell-LDA-1/2 versus the 2D surface BZ. The lowest-energy terminations of four different surface orientations are displayed (a) *a* plane, (b) *m* plane, (c) *c* plane, and (d) *r* plane. The left (middle, right) panel displays the PBEsol (PBEsol, shell-LDA-1/2) band structure for the unrelaxed (relaxed, relaxed) geometry. The 1×1 translational symmetry is kept for all surfaces. Surface bound states in the fundamental gap are displayed by blue solid lines, surface resonance states emerging from the gap into the projected bulk band regions are indicated by blue dashed lines.

the PBEsol exchange-correlation potential. The negative gap of bulk 2H-Ge in PBEsol generates an overlap of projected conduction and valence bands near Γ .

The slab bands in the projected fundamental gap region are governed by the original DB arrangement of a given surface. Small splittings of DB bands representing surface bound states result mainly from the finite slab thickness in the surface normal direction. These represent confinement effects with overlapping surface states decaying into the bulk region

and formation of “bonding” and “antibonding” combinations. Their splitting depends on the wave vector in the surface Brillouin zone. This effect is most pronounced for the *a*-plane surface but is also visible for the *c*-plane surface with one DB per surface unit cell near Γ .

QP effects are evident when comparing the middle and right panels in Figs. 6 and 7 for a given surface termination and relaxation. For semiconducting (or insulating) surfaces, the general behavior follows the expected widening of

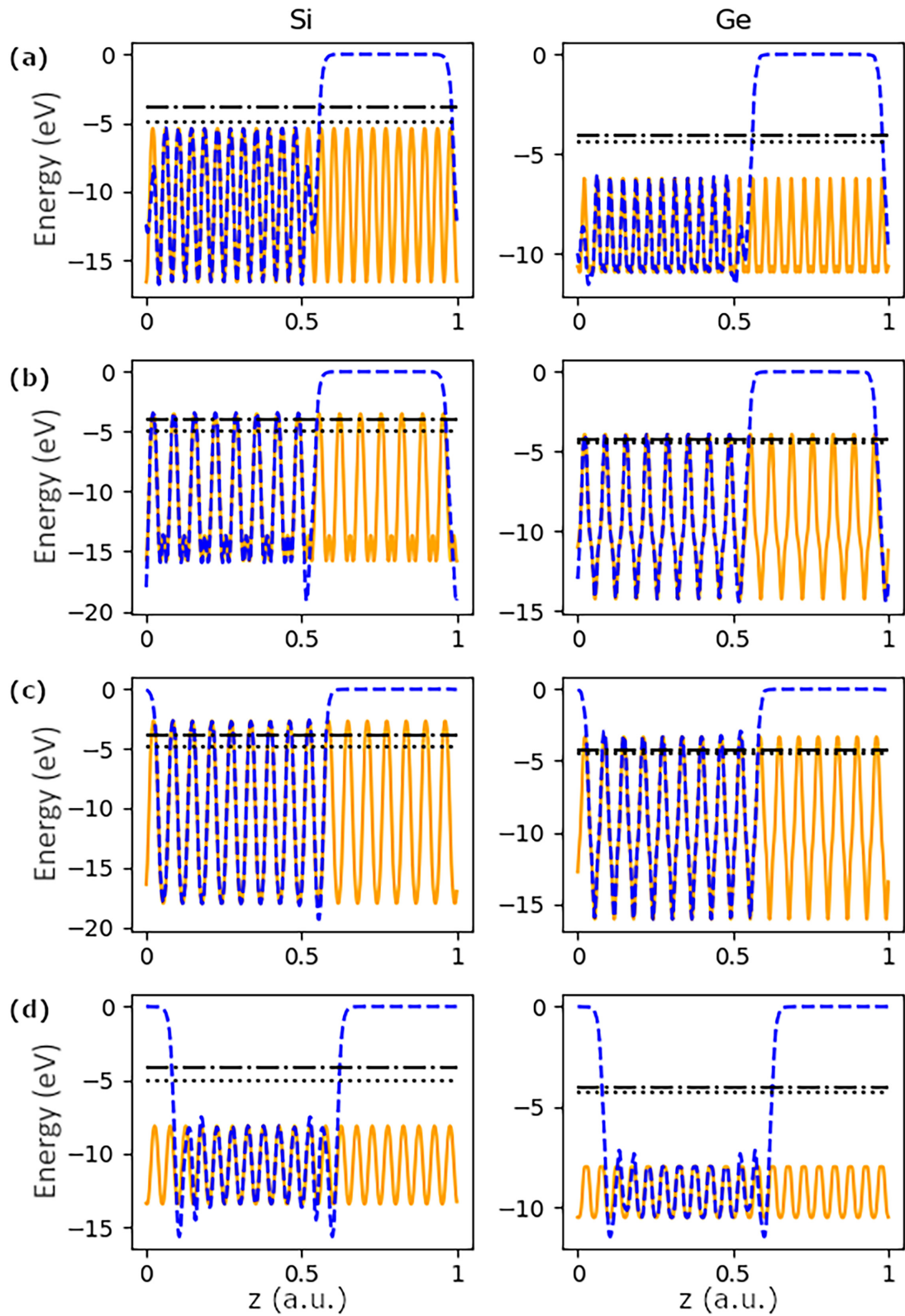


FIG. 8. Alignment of the plane-averaged electrostatic potentials $V(z)$ (with z in normal direction) of the slab and bulk calculations for four surface orientations (a) $[11\bar{2}0]$, (b) $[1\bar{1}00]$, (c) $[0001]$, and (d) $[1\bar{1}02]$ for hexagonal Si (left panels) and Ge (right panels). The vacuum level is taken as energy zero. The positions of the bulk ionization energies and electron affinities are indicated by the dotted and dash-dotted lines, respectively.

surface and bulk gaps by QP effects. For instance, in 2H-Ge, the overlap of conduction and valence bands around Γ in the projected bulk band structure disappears, and a gap of approximately 0.3 eV opens. For 2H-Si, the projected gap opens from approximately 0.3 to 1.0 eV. For gaps between empty and occupied surface bands, QP effects are similar but require more detailed discussion.

For hexagonal Si, the 1×1 surfaces of the four different orientations result in insulating band structures, at least after atomic relaxation—a trend reinforced by QP corrections. For hexagonal Ge, a clear surface gap opens only for the a and m planes. For the other two orientations, strong dispersion of surface bands combined with the small bulk gap leads to metallic surface band structures, while energetically well-separated upper and lower surface bands approach the Fermi level only near $\bar{\Gamma}$ (lower band) and $\bar{M}$ or $\bar{J}$ (upper band), the latter only for the r plane.

The predominant surface influence on band structure is visible from bands in the projected fundamental gap region. These bands are mainly related to DB-derived states that have changed their original sp^3 character after relaxation. For the a -plane surface in Figs. 6(a) and 7(a) with four surface atoms and four DBs, four surface bands appear in several regions of the surface Brillouin zone. Along the $\bar{J}\bar{M}$ high-symmetry line, two bands are degenerate for symmetry reasons. Even without relaxation, surface gaps appear between the two band pairs in this Brillouin zone region of approximately 0.7–0.8 (0.6) eV for Si (Ge). The upper empty surface bands result mainly from rehybridization of two neighboring sp^3 -like DBs with “rabbit ear”-like orientation into σ orbitals forming an occupied bridge bond and empty π orbitals, similar to dimer formation at (100) surfaces of cubic polymorphs [24]. The nearly empty and filled DB-derived bands are separated by vertical distances, e.g., the direct surface gap at $\bar{M}$, of approximately 1.6 (Si) and 1.7 (Ge) eV when QP corrections are included.

In the m -plane case [see Figs. 6(b) and 7(b)], only two DB-related surface bands appear, which are well separated energetically at least after relaxation. Both upper and lower DB-derived bands fade into the projected bulk band structure around $\bar{\Gamma}$, losing their bound state character. At the $\bar{M}$ point, the surface states of the upper band are mainly localized in p -like DB orbitals appearing at the sp^2 hybridized, inward-relaxed surface atom, while the occupied surface band relates to s -like orbitals at the outward-relaxed surface atom forming bonds to atoms beneath via p -like orbitals. QP effects are dramatic. The direct gap at $\bar{M}$ opens from 1.3 (0.1) to 1.8 (0.5) eV for Si (Ge). The indirect $\bar{\Gamma}\bar{M}$ gap opens from 0.1 to 0.6 eV for Si. In all cases, QP gap opening amounts to 0.5–0.7 eV.

The DB arrangement also governs the $(0001)1 \times 1$ surface. For the single-DB surface, only one band of surface bound states appears in the projected bulk fundamental gap around the Fermi level in the paramagnetic case [not shown in Figs. 6(c) and 7(c)]. Due to SOC inclusion, we investigate noncollinear spins. The lowest total energy of the c -plane surface is calculated for ferromagnetic DB occupation. Despite weak relaxation of surface geometry, magnetic exchange splitting between spin-up and spin-down DB bands in Figs. 6(c) and 7(c) opens a gap. At the $\bar{M}$ point of the 2D hexagonal

Brillouin zone, this splitting between empty and filled surface bands is approximately 0.8 eV for Si. With approximate QP corrections, this value increases significantly to 2.0 eV, again showing strong excitation effects.

The band structures for r -surfaces in Figs. 6(d) and 7(d) are more complex than those for other surfaces because each DB is responsible for a band of surface bound states. An occupied lone-pair band with weak dispersion appears near the valence band maximum. The empty p_z -like band with stronger dispersion appears in the upper part of the projected bulk fundamental gap. The two other DB-derived bands nearly merge into the lowest unoccupied or highest occupied bulk bands. The direct gap at $\bar{M}$ amounts to 0.8 (1.0) eV after atomic relaxation, while the indirect $\bar{\Gamma}\bar{J}$ gap is almost zero for Si and closed for Ge. QP effects also open the surface band structure of the Si r -plane surface significantly by 0.7 eV.

For all four surface orientations, we observe significant separation of the lowest empty and highest occupied surface bands for Si when considering QP effects in HSE06. This separation is highly reduced for Ge in LDA-1/2 due to a combination of the orbital character of the respective surface bands and the charge stripping of the LDA-1/2 method. For each facet, the character of both bands is predominantly p -like followed by some s character. Furthermore, the ratio between s - and p -like character of both bands is nearly identical. Since the charge stripping of the LDA-1/2 method for Ge is applied only to p -states, the two surface bands are shifted down by almost the same amount without widening the gap between them.

D. Ionization potentials and electron affinities

The characteristic electronic quantities of a semiconductor for electron emission or capture are the ionization potentials (IPs) and electron affinities (EAs), respectively. These quantities may depend on the surface facet at which the electronic processes occur [69]. The absolute magnitudes of IPs and EAs determine whether a semiconductor is a potential candidate for spontaneous water splitting under solar illumination through their relation to water reduction ($\text{H}_2/\text{H}_2\text{O} \cong 4.5$ eV) and oxidation ($\text{O}_2/\text{H}_2\text{O} \cong 5.73$ eV) levels measured with respect to the vacuum level [70].

The theoretical determination of IPs and EAs follows directly from the alignment of projected bulk band structures and slab band structures via their plane-averaged electrostatic potentials [55], as used to generate the band panels in Figs. 6 and 7. We illustrate the alignment procedure in Fig. 8. The projected bulk band structures with their conduction band minimum and valence band maximum (VBM) at Γ , as well as the slab band structures with their empty, fully occupied, or partially filled surface bands, allow the derivation of different electron affinities and ionization potentials. Besides the bulk values of A and I , which depend on surface structure and orientation via the actual electrostatic potential and still fulfill the definition of the bulk quasiparticle gap $E_g = I - A$, either corresponding surface values A_s and I_s (for insulating surfaces) or the work function $\Phi = A_s = I_s$ (for metallic surfaces) can be defined.

This procedure depends on the accuracy of the vacuum level and the alignment of bulk and slab band structures.

TABLE IV. Electron affinities A (A_s) and ionization potentials I (I_s) (in eV) for relaxed (1×1) Si and Ge surfaces with given orientation in HSE06 (Si) or shell-LDA-1/2 with HSE06-correction of the valence band edge (Ge) quality counting the position of the bulk extrema (extrema of surface bands) with respect to the vacuum level.

Surface	Si				Ge			
	I	I_s	A	A_s	I	I_s	A	A_s
a plane ($11\bar{2}0$)	4.9	4.7	3.9	4.5	4.4	4.6	4.1	4.3
m plane ($1\bar{1}00$)	5.0	5.0	4.0	4.4	4.4	4.5	4.2	4.3
c plane (0001)	4.8	4.8	3.8	4.2	4.5	4.6	4.3	4.6
r plane ($1\bar{1}02$)	5.0	4.9	4.1	4.4	4.3	4.4	4.0	4.3

It works well for Si using the HSE06 method. For shell-LDA-1/2 calculations of Ge structures, improvement of the incorrect Kohn-Sham band gap occurs only due to a significant downshift of the valence band edge and even a small downshift of the conduction band edge. Consequently, the distances between valence band edges and the vacuum level (and therefore the IPs and EAs) are skewed. This downshift can be compensated by aligning the valence band edge of the shell-LDA-1/2 bulk band structure with one computed using a self-consistent method, e.g., HSE06, and applying the same shift to the shell-LDA-1/2 surface slab electronic structures. Since the interband distances in the region surrounding the gap are almost identical between the two methods, the resulting IPs and EAs for both bulk and slab structures achieve pseudo-HSE06 accuracy without requiring such calculations of the slabs. We estimate the downshift-correction for hexagonal Ge between shell-LDA-1/2 and HSE06 to be approximately 1.4 eV.

For the surface that is most energetically favorable for a given orientation, we list the resulting electron affinities and ionization potentials in Table IV. The absolute values of bulk-like ionization energies and electron affinities vary by up to 0.3 eV between different orientations for each of the two hexagonal materials. This variation is attributed to the influence of different surface slab orientations used in the alignment procedure to obtain the vacuum level. Regardless, the bulk-like ionization energies $I = 4.8$ – 5.0 eV (4.3 – 4.5 eV) for Si (Ge) exhibit somewhat smaller values than experimental ones measured for the diamond structure: 5.10 – 5.33 eV (4.5 – 4.8 eV) [69,71]. However, the tendency of smaller Ge ionization energies compared to Si is confirmed with the same order of approximately 0.5 eV as found in experimental values. Previous calculations of I and A are available only for the c -axis orientation within the MBJLDA approach. The values $I = 4.88$ (4.48) eV and $A = 3.85$ (4.16) eV have been calculated for 2H-Si (Ge) [49]. These calculations also suggest larger values $I = 5.22$ (4.54) eV for the cubic polytype 3C-Si (Ge).

IV. CONCLUSIONS

We have presented a comprehensive first-principles study of atomic relaxation and electronic structure for low-index surfaces of the most important hexagonal (lons-

daleite) polytypes of silicon and germanium: 2H-Si and 2H-Ge.

To optimize the atomic structure, we performed calculations within density functional theory using the semilocal exchange-correlation functional PBEsol. We considered four surface orientations with one (a plane), two (m plane), four (r plane), and two (c plane) different terminations.

Among the relaxed surface geometries that preserve 1×1 translational symmetry, we found a clear energetic ordering of surfaces with their most stable terminations. For the surface excess energies of the relaxed favorable terminations, we established the sequence $\gamma_m < \gamma_a < \gamma_r < \gamma_c$ for both group-IV polytypes 2H-Si and 2H-Ge. We have discussed the consequences of this energetic ordering for the morphology of possible nanocrystallites and favorable facets of hexagonal nanowires.

We investigated the electronic structure of the a -, m -, c -, and r -plane surfaces within the framework of approximate quasiparticle approaches, combining HSE06 calculations for Si and shell-LDA-1/2 calculations for Ge. The resulting bands of surface bound states within the projected fundamental gaps of the bulk polytypes are governed by dangling bonds, whose hybridization reflects the vertical and lateral displacements of surface atoms. Of particular interest is the formation of a gap between empty and filled surface bands for the a - and m -plane cases. In contrast to these insulating surfaces, the relaxed (0001) 1×1 surface with only one dangling bond per surface atom exhibits two surface bands when its spin orientation leading to ferromagnetic surface character is considered. In general, our results support the concept of a general tendency for gap opening through atomic and electronic relaxation effects following excitation of the surface electronic system.

The alignment of slab band structures and projected bulk band structures via slab and bulk electrostatic potentials enables measurement of the distances between the energetically highest occupied and lowest empty electronic states of surface or bulk, yielding ionization potentials and electron affinities. The ionization potentials of silicon are larger by approximately 0.5 eV compared to germanium. This tendency agrees with measured ionization potentials for diamond structures, although hexagonal surfaces appear to exhibit smaller absolute values.

Our study provides fundamental insights into the surface properties of hexagonal group-IV semiconductors, establishing a foundation for understanding their potential applications in optoelectronic devices. The observed surface energy hierarchy and electronic properties offer valuable guidance for the design and synthesis of hexagonal Si and Ge nanostructures with tailored surface characteristics. Furthermore, knowledge of surface stability is essential for determining suitable growth substrates and optimizing epitaxial conditions for high-quality hexagonal thin-film synthesis.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX: SURFACE ENERGY CONVERGENCE WITH NUMBER OF LAYERS

Studies of the size of surface slabs necessary for convergence of the surface energy have been conducted for cubic Si and Ge [20] in the past. For hexagonal Si and Ge we have performed our own test calculations with varying numbers of atomic layers, which we present in Table V.

TABLE V. Surface energies (in meV/Å²) of unrelaxed *c*-plane hexagonal Ge and Si slabs with increasing slab size.

No. layers	Ge	Si
8	79.06	106.22
12	79.22	106.24
14	79.16	106.44
16	79.27	106.41
18	79.23	106.48
20	79.18	106.47
22	79.26	106.48
24	79.18	106.46
28	79.18	106.46
32	79.19	106.47
36	79.18	106.47

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