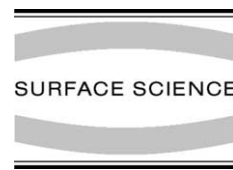




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New electron states that float on semiconductor and metal surfaces

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Abstract

We report first-principle electronic-structure calculations using the local density approximation in the density functional theory for Si(100) and Al(100) surfaces. We find a novel class of surface electron states that are distributed not near atomic arrays but float around with the maximum amplitudes being substantially separated from matters. We also find that the origin of the unusual character is quantum spill of electron density from matters and exchange-correlation effects among electrons.

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Electron states in condensed matters with translational symmetry generally extend in whole systems satisfying the Bloch theorem. Introduction of imperfections in the matters then causes mixing of the Bloch states and thereby induces localized states: point and line defects (e.g. vacancies, interstitials and dislocations) induce particular electron states of which wavefunctions (WFs) are localized near the defects. Surfaces are also regarded as pla-

ner imperfections. WFs of surface states are indeed distributed in the surface regions. All these electron states, despite the different characteristics, possess a common feature: the WFs have more or less a character of atomic orbitals of constituent elements.

A different class of electron states has been found in some cases: in layered materials such as graphite or hexagonal boron nitride (*h*-BN), there are peculiar electron states of which WFs are distributed not near atomic sites but in the interlayer regions [1–5]; similar states are also found to emerge in carbon nanotubes [6,7] and in boron-nitride nanotubes [8,9] with the maximum electron

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density inside or outside of the atomic walls of the tubes. It has been clarified [6,7] that the WFs of those states extend like nearly free electrons (NFE) in regions where atoms are absent. A similar NFE state is also found in supercritical water [10]. Those states are unoccupied in usual cases. Yet they are located below the vacuum level and play decisive roles in excitation spectrum [2] and even in ground-state electronic properties upon intercalation of foreign atoms or clusters in the spacious materials [11,12]. The origin of those unusual states is unclear at present, however.

In this Letter, we perform total-energy electronic-structure calculations for silicon and aluminum surfaces. We find that unusual electron states, irrespective of chemical elements or geometrical models, of which WFs distribute above the surfaces with the absolute value being maximum substantially far from atomic sites emerge below the vacuum level. Analysis of calculated results leads to a conclusion that the origin of the unusual states is the quantum spill of electron charge densities and exchange-correlation effects among electrons. We argue that there is a new class of electron states in polyatomic systems: their WFs *float* in the vicinity of atomic arrays or in the space inside the matters.

All calculations were performed based on the density functional theory [13,14]. We use the local density approximation to treat the exchange-correlation energy of interacting electrons [15,16]. Norm-conserving pseudopotentials with separable forms are adopted to describe the electron-ion interaction [17,18]. In the present study, we chose (100) surfaces of Al and Si as representatives of metal and semiconductor surfaces, respectively. The Si and Al surfaces are simulated by repeating slab models with 4, 6, 7, and 8 atomic layers and 3, 5, 7, 9, and 19 atomic layers, respectively. Each slab is separated by 24 Å-vacuum regions to analyze the electron states possessing a *floating* character. In Si(100), outermost atoms on both surfaces of all slabs are not terminated by H atoms and thus form asymmetric dimers. To simulate thicker slabs, we also study the 8-atomic-layer Si slab with H atoms in which each of the bottom-most Si atoms is terminated by two H atoms. We use 1×1 and 4×4 lateral periodicities for the Al

and Si surfaces, respectively. The valence WFs of both Si and Al are expanded in terms of the plane-wave basis set with the cutoff energy of 9 Ry. Geometry optimization is performed for all the atoms in the slabs, except for the case of the 8 atomic-layer Si slab with hydrogen atoms in which the bottom-most Si and H atoms are fixed during the structural optimization. We use the conjugate-gradient minimization scheme both for the electronic structure calculation and for the geometry optimization [19]. In the optimized geometries the remaining force acting on the atoms is less than 0.005 Ry/Å.

Fig. 1(a) shows the total valence electron charge density of the Si(100) surfaces using the slab with 8 atomic layers. We observe that a small but substantial portion of charge is quantum-mechanically spilled from the atomic array of the slab. This infers that an additional electron placed in the spilled electron distribution feels an attractive potential and thus may be accommodated in a peculiar electron state below the vacuum level. We have examined the wavefunctions (Kohn–Sham orbitals) of all the electron states (Fig. 1(b)) of the present Si slab. Most of the WFs are found to be distributed in the atomic array of the slab. Yet we have found a peculiar electron state labeled α in Fig. 1(b) at 4.66 eV above the Fermi level E_F . An unusual feature of the WF of α is shown in Fig. 1(c): along the direction perpendicular to the surface, there are several nodes and peaks; the outermost node and peak are located clearly at the space outside the slab where the Si atoms are absent; the outer most peak is located at 2 Å above the surface atomic array; in the lateral plane the state is two-dimensionally extended along the surface (Fig. 1(c)). The characteristics of the WF of the α state is similar to those of the interlayer states of graphite and *h*-BN. The present results indicate that quantum spill of electron density induces peculiar electron states of which WFs float around the atomic arrays of the matters: *floating states*.

Table 1 shows the slab-thickness dependence of the energy level of the floating state on the Si(100) surfaces. We find that the energy level is rather insensitive to the slab thickness: the level is located at about 4.5 eV above E_F . For all slabs, the WF of the floating state is distributed outside the atomic

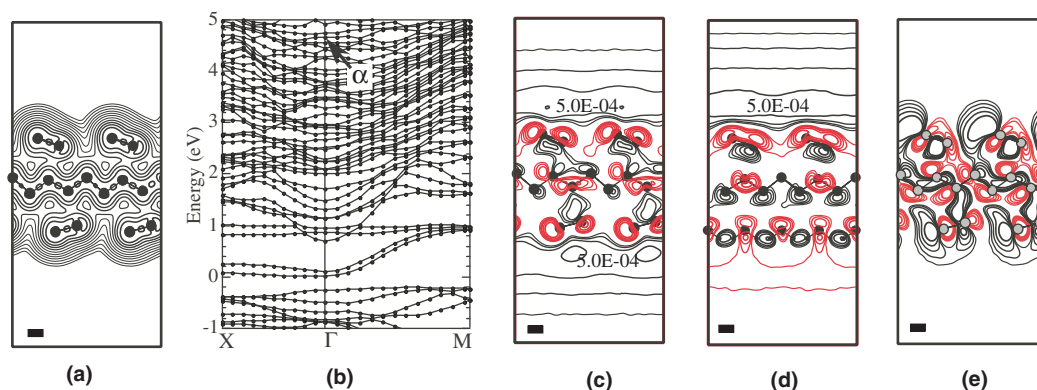


Fig. 1. (a) Contour plot of electron charge density in the slab of the 8 Si atomic layers with (100) surfaces. Solid circles denote the atomic position. (b) Energy bands of the 8 Si atomic layers with (100) surfaces. The origin of the energy scale is the Fermi level. (c) Contour plot of the WF of the floating state (see text) at Γ point for Si slab with 8 atomic layers, and (d) that for Si slab with H atoms. (e) Contour plot of the WF of the unoccupied state (see text) at Γ point for Si slab with 8 atomic layers. Black and red lines correspond to the positive and negative values of the WFs. In (c) and (d), the contour lines corresponding to the maximum amplitude, 5.0×10^{-4} [$e/(a.u.)^3$], are attached by the numbers. Each contour represents twice (or half) the amplitude or the density of the adjacent contour lines. Length of bars corresponds to 2 Å.

Table 1

Kohn–Sham energy level of the floating state (E_{float}) in the Si slabs with (100) surfaces for various thicknesses

Atomic layers	4	6	7	8	8H
E_{float} (eV)	4.39	4.52	4.55	4.66	4.80

Kohn–Sham energy level of the floating state (E_{float}) in the Si slab of which the bottom-most Si atoms are saturated by H atoms (8H) is also listed. Energies are measured from the Fermi level.

array with the absolute value being maximum at 2 Å far from the top-layer surface atomic plane. For comparison, we show the WF of another state energetically near the floating state (Fig. 1(e)). The energy level of the state is 5.09 eV above E_{F} . In contrast to the floating state, it has a character of atomic orbitals and is distributed near atomic sites.

For the 4-atomic-layer slab, the energy level of the floating state becomes deeper by more than 0.1 eV. This is a consequence of structural modification in ultrathin films: The calculated amount of the buckling of surface dimer atoms for the 4-layer slab is 0.21 Å which is considerably smaller than those for the other slabs (about 0.7 Å); as a result, the potential profile in lateral planes outside the atomic array and then the WF of the floating state become flatter, thereby reducing the kinetic energy.

Since the work function of the Si surfaces is about 5 eV, the floating state is essentially bound below the vacuum level. Analysis of the WFs also corroborates the bound nature of the floating state: Other WFs of the upper-energy states are found to extend in the whole simulation cell, not exhibiting the floating characteristics above the surface.

Another slab in which the bottom Si atoms are terminated with hydrogen atoms and then the bottom-most Si and the H atoms are fixed at ideal lattice sites may simulate the situation in thicker slabs. Also, the H-decorated slab is a representative of chemically decorated semiconductor surfaces. It is important to examine whether the floating state emerges or not on such surfaces. We have thus performed total-energy electronic-structure calculations for the 8-atom-layer Si(100) slab with each bottom-most Si terminated with 2 H atoms. We have indeed found a floating state in this slab. The WF of the floating state is shown in Fig. 1(d). The distribution of the WF is quite different in the vicinity of the H-attached surface. At the H-terminated surface, the floating states do not emerge on the surface, since the H atoms prevent the quantum spill of electrons of surface Si atoms. Yet it is clear that there is also a peculiar electron state which has a character of floating

state. The energy level of the state is located at 4.8 eV above E_F (Table 1) which is still lower than the vacuum level. This finding corroborates that the unusual floating state is certainly inherent to semiconductor surfaces.

We next study electronic structures of the Al(100) surfaces in order to examine whether floating states exist on metal surfaces. Fig. 2(a) shows the electronic energy bands of the Al(100) surface obtained by using the slab consisting of 11 Al atomic layers. Again we have explored the WFs of all the electron states and found a state α in Fig. 2(a) that has the floating character. Fig. 2(b) shows the WF distribution of the state α . It is clear that the state is extended in lateral planes. In the direction perpendicular to the surface it has nodes and peaks and the outer-most peak is located at about 2 Å above the surface atomic array. The electron charge density (Fig. 2(c)) clearly shows quantum spill from the atomic array with substantial density at the peak position of the floating state. Obviously, the distribution is similar to those of the interlayer states in graphite and of the floating state on the Si surfaces. Calculated value of the Kohn–Sham energy level of the state is 3.4 eV above E_F so that the state is located below the vacuum level (the work function on the Al(100) is 4.41 eV [20]). We thus conclude that

the quantum spill of electron density from atomic arrays of matters induce peculiar electron states of which WFs float on surfaces of the matters which-ever semiconducting or metallic the matters are.

In Table 2, we show the Kohn–Sham energy level of the floating state on Al(100) surfaces for various slab thicknesses. The energy level of the state is found to lie always at about 1 eV below the vacuum level. Furthermore, the outer-most peak of the WF is located at about 2 Å above the surface, and the peak position is insensitive to the slab thickness. We have also done the calculation for the Al slab of 19 atomic layers. For this sufficiently thick slab, we have found that the floating state also emerges below the vacuum level (Table 2).

For metal surfaces, it has been known that amounts of the spilled electron densities outside the atomic slabs are changing by varying the electron density inside the slab: The spilled amount increases with decreasing the parameter r_s [$\rho = 3/(4\pi r_s^3)$] [21]. We have therefore calculated the distribution of the floating-state WF under various lattice parameters and thus various r_s parameters for Al slabs with three atomic layers. The outer-most peak position in the direction perpendicular to the surface is shown in Fig. 3. The peak position gradually approaches to the surface by decreasing

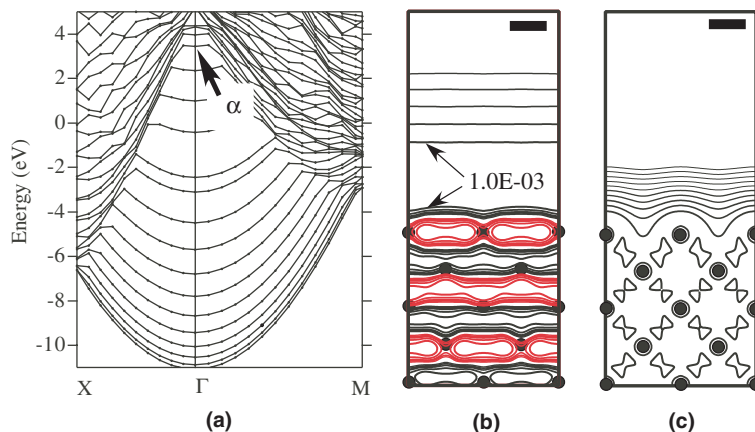


Fig. 2. (a) Energy bands of the Al(100) surfaces. Energies are measured from the Fermi level. Contour plot of (b) the WF of the α state at Γ point and (c) the electron charge density of Al(100) surfaces. Solid circles denote the atomic position of Al atoms. Black and red lines correspond to the positive and negative values of the WF. In (b), the contour lines corresponding to the maximum amplitude, 1.0×10^{-3} [$e/(\text{a.u.})^3$], are attached by the numbers. Each contour represents twice (or half) the amplitude or the density of the adjacent contour lines. Length of bars corresponds to 2 Å.

Table 2
Kohn–Sham energy level of the floating state (E_{float}) in the Al slabs with (100) surfaces for various thicknesses

Atomic layers	3	5	7	9	11	19
E_{float} (eV)	3.81	3.19	3.63	3.82	3.44	3.45

Energies are measured from the Fermi level.

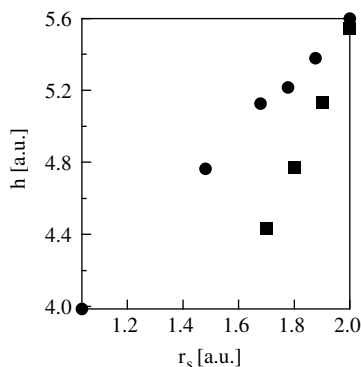


Fig. 3. r_s dependence of the peak position (h) of the floating state for the Al slab (solid circles) and for the jellium slab (solid squares) [$\rho = 3/(4\pi r_s^3)$]. The origin of the peak position is the topmost atom of the Al surface.

the lattice parameter. This feature is due to the increase of the amount of the spilled electron density and the resulting enhancement of the attractive potential above the surface. The positive background charge of the slab is not screened by the electrons inside the peak position of the floating

state because of the finite distribution of the spilled charge outside the position.

In order to further elucidate the nature of the floating state, we now perform the calculations for simple slabs in which nuclei are replaced by uniform positive background charge. We first examine a slab which has the width of $d = 4$ [a.u.] and is filled with electrons with $r_s = 2$ [a.u.]. We use local density approximation for the exchange–correlation potential for the interacting electrons [15,16]. In this simple slab, the WF is decoupled in a lateral-plane part and a remaining part $\phi(z)$ in z direction perpendicular to the surface. The calculated $\phi(z)$ along with the eigenvalues and the total potential is shown in Fig. 4(a). The Fermi level is situated in the second subband of which $\phi(z)$ has a single node at the center of the slab. The third and the fourth subbands are empty but the bottom of those unoccupied subbands are below the vacuum level. The $\phi(z)$ for the third and fourth subbands has the outermost peak outside the slab and then decays in vacuum. This feature that the WF is neither bound in the slab nor extended in vacuum is characterized as *floating*.

We have also performed the calculations for different r_s 's and the calculated outermost peak-position of $\phi(z)$ is plotted as a function of r_s in Fig. 3. It is found that the peak approaches to the boundary of the slab with decreasing r_s as in the case of the Al slabs. On the other hand, the floating character disappears when we add additional flat

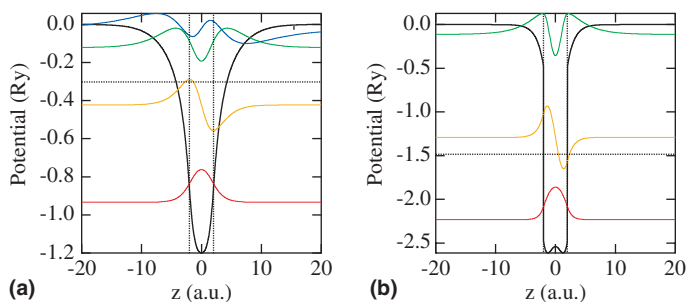


Fig. 4. (a) Wavefunctions $\phi(z)$ and the total potential in the perpendicular direction for a slab of the width of 4 [a.u.] and with positive uniform background charge. (b) Same with (a). But an additional attractive flat potential with the amount of $V = -2$ Ry is added. Black line denote the total potential energy. Red, tangerine, green, and blue lines denote $\phi(z)$ of the ground, the first excited, the second excited, the third excited, and the fourth excited states, respectively. The location of each $\phi(z)$ corresponds to the position of each energy level. Dotted horizontal and vertical lines denotes the Fermi level energy and the boundaries of the slab, respectively.

attractive potential with the amount of $V = -2$ Ry (Fig. 4(b)). The additional potential draws the electron density inside the slab. Consequently the third subband loses the floating character, becoming almost bound, and the fourth subband is extended with the energy above the vacuum level. This corroborates the statement that the floating character is caused by the quantum spill of the electron density out of the slab.

We now recognize that quantum spill of electrons is important how the floating character comes up. The exchange energy is also expected to play a role since it may cause downward shift of the Kohn–Sham level. We thus perform electronic structure calculations for the Al slab with 11 atomic layers and for the jellium slab using only the Hartree approximation. It is found that the floating states lose their character and become extended states with the orbital energies above the vacuum level. Hence the exchange–correlation energy in addition to the spill of the electron density plays a decisive role in the appearance of the floating state. These facts indeed corroborate that the floating state is originated from only the quantum spill of electron density from matters and their interaction. Therefore, the state is completely different from the other surface states which emerge outside the matter such as image potential states.

The floating states on the metal and semiconductor surfaces are located at about 3–4 eV above the Fermi level and is detectable by using spectroscopic experiments. On the other hand, it is known that the energy levels of the interlayer states of the graphite intercalation compounds (GICs) significantly shift downward due to the attractive potential of charged alkali atoms [1]. It is thus expected that the floating states on the metal and semiconductor surfaces also shift downward upon adsorption of positively charged ions or molecules, and affect the surface electronic properties. Also, it is recently recognized that the intratube states hybridize with atomic orbitals upon insertion of fullerenes and that the Fermi-level density of states drastically changes [12,22]. Hence, the floating

state would play an important role in adsorption of atoms and molecules on the surfaces, since hybridization between the states and the molecular/atomic states of the adsorbates is expected. Further, carriers are injected in the floating state, for instance, they should exhibit the high mobility on the surfaces since the state is extended in the lateral plane and floats from the scatterers in the atomic arrays.

Acknowledgements

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