Quantum oscillations in adsorption energetics of atomic oxygen on Pb(111) ultrathin films: A density-functional theory study

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Abstract

Using first-principles calculations, we have systematically studied the quantum size effects of ultrathin Pb(111) films on the adsorption energies and diffusion energy barriers of oxygen atoms. For the on-surface adsorption of oxygen atoms at different coverages, all the adsorption energies are found to show bilayer oscillation behaviors. It is also found that the work function of Pb(111) films still keeps the bilayer-oscillation behavior after the adsorption of oxygen atoms, with the values being enlarged by 2.10~2.62 eV. For the diffusion and penetration of the adsorbed oxygen atoms, it is found that the most energetically favored paths are the same on different Pb(111) films. And because of the modulation of quantum size effects, the corresponding energy barriers are all oscillating with a bilayer period on different Pb(111) films. Our studies indicate that the quantum size effect in ultrathin metal films can modulate a lot of processes during surface oxidation.

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I. INTRODUCTION

Because of the well-defined simple geometry, thin metal films that are nanometers thick provides an ideal system to study the quantum behaviors of electrons in reduced dimensions. Many researches have been carried out to investigate the corresponding quantum size effect (QSE) [i.e., the dependence on the film thickness] on electronic properties of metal films. According to the “particle-in-a-box” model, the itinerant electrons confined in metal films are quantized into discrete energy levels along the \( z \) direction perpendicular to the film surface, giving rise to the so-called quantum well states (QWS) \[1, 2, 3, 4, 5, 6, 7, 8\], while the energy dispersion in the \( xy \) direction remains parabolic, forming a series of energy subbands. As the thickness of the metal film increases, these subbands sequentially cross the Fermi level, and make the physical properties of metal film oscillate periodically. Among all the metal species, ultrathin Pb(111) films have attracted vast attentions. By employing the epitaxy depositing methods, atomically flat Pb(111) films can be perfectly fabricated on both metal \[9\] and semiconductor \[10, 11\] substrates. Moreover, extensive knowledge of the electronic properties and crystallite shape have been attained through systematical investigations. Prominently, it has been found that the electron Fermi wavelength of Pb is nearly four times the lattice spacing along the [111] direction, so most physical properties of Pb(111) films such as the thermal stability, surface energy and work function, all oscillate with the thickness in a quasi-bilayer period \[8, 10, 12\]. The quantum effect of ultrathin Pb(111) films can also result in a spectacular oscillatory superconductivity transition temperature, by modulating the electron density of states near the Fermi level and the electron-phonon coupling \[13\]. Based on these previous results, it is easily understood that besides these intrinsic physical properties, QWS of ultrathin Pb(111) films will also affect the surface reactions such as oxidation.

In fact, a lot of researches have been carried out recently to study QSE on surface reactivities. Most of these studies are for applications in catalysis, corrosion, and gas sensing. For example, the lifetime of negative \( \text{N}_2 \) ions physisorbed on Ag(111) films \[14\] and the desorption temperature of CO on Cu(100) films \[15\] are both found to be modulated by the film thickness. Apart from other reactivities, the oxidation of metal surfaces needs special concerns since the formed metal oxide layers have dominated many crucial properties of metals in industrial applications \[16, 17\]. Previous experimental studies have already
revealed that the initial oxidation rate of Mg(0001) \[18\] and Pb(111) films \[19\] depends on the film thickness in an oscillatory way. So it is of high interests to theoretically investigate the specific mechanisms of the oxidation processes and how QSE influences the initial oxidation rate. For the Mg(0001) system, unfortunately, present theoretical studies have failed to explain its surface oxidation process. The most notable is the long-term enigma of low initial sticking probability of thermal O\(_2\) molecules at Mg(0001), which has been measured by many independent experiments \[18, 20\] but cannot be reproduced by adiabatic state-of-the-art density functional theory (DFT) calculations \[21\]. The central problem is that the adiabatic DFT calculations were unable to find any sizeable barriers on the adiabatic potential energy surface (PES), whose presence, however, is essential for explanation of the experimental finding. This has led to speculations that nonadiabatic effects may play an important role in the oxygen dissociation process on the Mg(0001) surface. For the Pb(111) system, fortunately however, the oxygen dissociation process can be reasonably understood based on the adiabatic DFT calculations. In fact, our previous studies have already revealed that there are precursor adsorption states for molecular O\(_2\), and the molecular adsorption energy of O\(_2\) shows a bilayer oscillation QSE with the thickness of Pb(111) films \[22\]. Moreover, we have also studied the adsorption properties for atomic O both at surface and subsurface sites systematically \[23\].

Based on these results, we further study the QSE on the adsorption energies and diffusion energy barriers of oxygen atoms on Pb(111) films in this work. The rest of the paper is arranged as follows. In Sec. II we give details of the first-principles total energy calculations, which is followed in Sec. III by our results of QSE on the adsorption energy for on-surface and subsurface adsorption of oxygen atoms. In Sec. IV, the QSE on the diffusion and penetration of oxygen atoms on Pb(111) films is discussed. And finally, we give our conclusions in Sec. V.

II. COMPUTATIONAL METHOD

The DFT total energy calculations are carried out using the Vienna \textit{ab initio} simulation package \[24\]. The generalized gradient approximation (GGA) of Perdew \textit{et al.} \[25\] and the projector-augmented-wave (PAW) potentials \[26\] are employed to describe the exchange-correlation energy and the electron-ion interaction, respectively. The so-called “repeated
slab” geometries [27] are employed to model the clean Pb(111) films ranging from 3 to 25 monolayers (ML). A vacuum layer of 20 Å is adopted to separate the Pb(111) slabs in two adjacent cells, which is found to be sufficiently convergent from our test calculations. The oxygen atoms are placed on both sides of the slabs in a symmetric way. During our calculations, the positions of all lead layers as well as the O atoms are allowed to relax until the forces on them are less than 0.02 eV/Å. The plane-wave energy cutoff is set to 400 eV. A Fermi broadening [28] of 0.1 eV is chosen to smear the occupation of the bands around E_F by a finite-T Fermi function and extrapolating to T=0 K. Integration over the Brillouin zone is done using the Monkhorst-Pack scheme [29] with 21 × 21 × 1 grid points at Θ=1.0 coverage and 13 × 13 × 1 grid points at Θ=0.25 coverage. The calculated lattice constant of bulk Pb is 5.03 Å, in good agreement with the experimental value of 4.95 Å [30]. Furthermore, the nudged elastic band (NEB) method [31] is used to find the minimum energy path and the transition state for O atoms to penetrate or diffuse on ultrathin Pb(111) films.

One central quantity tailored for the present study is the average binding energy of the adsorbed oxygen atom defined as

$$E_b(Θ) = -\frac{1}{N_O}[E_{O/Pb(111)} - E_{Pb(111)} - N_OE_O],$$

where $N_O$ is the total number of O adatoms present in the supercell at the considered coverage Θ (we define Θ as the ratio of the number of adsorbed atoms to the number of atoms in an ideal substrate layer). $E_{O/Pb(111)}$, $E_{Pb(111)}$, and $E_O$ are the total energies of the slabs containing oxygen, of the corresponding clean Pb(111) slab, and of a free O atom respectively. According to this definition, $E_b$ is also the adsorption energy $E_{ad}$ per O atom, i.e., the energy that a free O atom gains upon its adsorption. Thus a positive value of $E_b$ indicates that the adsorption is exothermic (stable) with respect to a free O atom and a negative value indicates endothermic (unstable) reaction.

On the other hand, since in most cases, the oxygen chemisorption process inevitably involves the dissociation of O_2 molecules, thus the adsorption energy per oxygen atom can alternatively be referenced to the energy which the O atom has in the O_2 molecule by subtracting half the dissociation energy $D$ of the O_2 molecule,

$$E_{ad(1/2O_2)} = E_b - D/2.$$  

With this choice of adsorption energy, then a positive value indicates that the dissociative
adsorption of $O_2$ is an exothermic process, while a negative value indicates that it is endothermic and that it is energetically more favorable for oxygen to be in the gas phase as $O_2$. The binding energy of spin-polarized $O_2$ is calculated to be $D=5.78$ eV per atom and the O-O bond length is about $1.235 \, \text{Å}$. These results are typical for well-converged DFT-GGA calculations. Compared to the experimental \cite{32} values of 5.12 eV and 1.21 Å for O binding energy and bonding length, the usual DFT-GGA result always introduces an overestimation, which reflects the theoretical deficiency for describing the local orbitals of the oxygen. We will consider this overbinding of $O_2$ when drawing any conclusion that may be affected by its explicit value.

III. QUANTUM SIZE EFFECT ON THE ADSORPTION ENERGY OF ATOMIC OXYGEN

First, we do geometry optimizations for clean ultrathin Pb(111) films with different thickness. This is necessary both for verification of numerical reliability and for comparison with adsorbed cases. The results for various physical quantities display well-defined QSE, which is fully consistent with previous first-principles report \cite{8}, thus suggesting that the present calculation is reliable and accurate.

Formally, there are four high symmetry sites for surface adsorption, i.e., the top, bridge (bri), hcp, and fcc sites, which are schematically shown in Fig. 1(a). In our previous study \cite{23}, we have found that the top site is notably less favorable than the fcc and hcp hollow sites. When the O atom is placed on the bridge site, it always moves to the fcc hollow site after relaxation. Actually, Fig. 6 below will show that the bridge site is a saddle point in the O diffusion path from hcp to fcc site. Combining with our another calculated result that after dissociation of $O_2$ along the most stable channel, the two O atoms will occupy the surface fcc and hcp hollow sites, respectively, we derive that these two surface sites are most relevant and accessible for experimental observation. Thus, our present numerical calculation of QSE on surface adsorption is focused on the surface fcc and hcp hollow sites.

Our calculated adsorption energies for the surface adsorption at the fcc hollow site with the coverage of $\Theta=1.0$ ML are shown in Fig. 2. Because of the similarities with the results at surface fcc hollow site, the calculational results for the adsorption energies at surface hcp hollow site will not be presented and discussed. One can see from Fig. 2 that the adsorption
energy mostly oscillates with the film thickness in a bilayer period. However, this bilayer oscillation is interrupted by a crossover at the film of 15 MLs, which is noted as a beat in the bilayer oscillation behaviors and comes from the slight difference between the electron Fermi wavelength of Pb and four times of the lattice spacing along the [111] direction \[33\]. In our calculations, we see that the bilayer oscillation persists for films as thick as 21 MLs.

Between adsorbate and substrate, many physical properties such as binding (adsorption) energy, amount of charge transfer, and work function of the adsorption system change significantly with coverage. So studying the change of these quantities at different coverage has become one hot point. In this paper, our focus is to explore the QSE modulating the materials’ basic physical properties. But we are still not very clear whether the oscillating behaviors of materials’ basic physical properties are changed at different oxygen coverage. So, to get more detailed information about this problem, we also calculate the surface adsorption energy of atomic oxygen at the coverage of \(\Theta = 0.25\) ML, as a comparison with the results at the coverage of \(\Theta = 1\) ML.

The calculated adsorption energy for the on-surface adsorption at the 0.25 ML coverage is shown in Fig. 3. One can see that the adsorption energy also oscillates with the film thickness in a bilayer period. The difference from the result for the 1 ML coverage lies in that the adsorption energy for the 0.25 ML coverage has a crossover at the film of 10 MLs, and the oscillation orientation of the adsorption energy is reversed for Pb(111) films of 3 to 11 MLs. For Pb(111) films beyond 11 MLs, the bilayer-oscillation orientation becomes the same, which is very interesting.

Another central concern for the adsorption of atomic species is the change of the electronic structures of metal surfaces. So we here further calculate the influence on the work function of Pb(111) films from the adsorption of oxygen atoms. As shown in Fig. 4, the work function of clean Pb(111) films oscillates with a bilayer period, and encounters two crossovers at 4 and 13 MLs. This phenomenon is identified as a 9-ML beating envelope on which the bilayer oscillation is superimposed, and has been observed for a lot of electronic properties of Pb(111) films. For example, the beating on the bilayer oscillation of the surface energy happens at 8 and 17 MLs \[8\], and that of the density of states at the Fermi energy happens at 6 and 15 MLs \[19\]. After the 1 ML on-surface adsorption of oxygen atoms, we can see from Fig. 4 that the work function is enlarged by 2.10 ~ 2.62 eV for all Pb(111) films. It means that the surface electrons will encounter a higher energy barrier to penetrate into the
vacuum layer. Although the values are enlarged, we see that the work function still remains the bilayer oscillation behavior after the adsorption of oxygen atoms, which is almost the same as the oscillation behavior in the work function of clean Pb(111) films. Therefore, we deduce that the change of the work function caused by the adsorption of oxygen atoms is hardly influenced by the QSE of different Pb(111) films.

In parallel with the surface adsorption, we also calculate the QSE on the adsorption energy for the subsurface adsorption of atomic oxygen. As shown in Figs. 1(b)-(d), there are three different high-symmetry sites for oxygen occupation in subsurface region. The octahedral site (henceforth octa) lies just underneath the on-surface fcc site, and one tetrahedral site (tetra-I) lies below the on-surface hcp site. A second tetrahedral site (tetra-II) is located directly below a first-layer metal atom. From the calculated adsorption energies, we reveal that the most preferred adsorption site for the oxygen atom is the tetra-II site, in a wide coverage range \[23\]. In fact, the adsorption state at the tetra-II site is also found to be the most stable one in both surface and subsurface adsorption states \[23\]. Therefore, to study the QSE on the adsorption energy of the tetra-II adsorption state is very meaningful. Similar to the surface adsorption, the subsurface adsorption energy for atomic oxygen is also larger at a higher coverage \[23\]. So we here focus on the QSE for the 1 ML subsurface adsorption of oxygen atoms.

The result of the adsorption energy for subsurface oxygen is shown in Fig. 5 as a function of the thickness of Pb(111) films, from which one can clearly see a bilayer oscillation fashion. The oscillation is interrupted respectively at the 7 and 16 MLs, proving the existence of the 9-ML beating envelope. Although the bilayer oscillation and the beating envelope are normal characters for a lot of electronic properties of Pb(111) films, our calculational results are in fact a little fortuitous, because the unconfined \( p_x \) and \( p_y \) states of Pb also take part in the electronic interactions with O atoms \[23\]. And we are not surprised that the beating behavior for the subsurface adsorption of oxygen atoms does not accord well with that observed in surface oxidation \[19\]. During the subsurface adsorption of O atoms, the work function of Pb(111) films is found to be lowered down by about \( 0.65 \sim 1.04 \) eV.
IV. QUANTUM SIZE EFFECT ON THE DIFFUSION AND PENETRATION OF ATOMIC OXYGEN

Diffusion of oxygen atoms after dissociation is also an elementary process during the whole surface oxidation process. Understanding the diffusion process is also very important for many important catalytic reactions such as oxidation of CO and hydrocarbons. So we here present first-principles calculations to study the QSE on the diffusion energy barriers of oxygen atoms on different Pb(111) films. In our previous work, we have reported that the diffusion energy barrier is always larger for higher coverages adsorption of oxygen atoms [23]. And so we here mainly focus on the QSE on the diffusion of surface oxygen atoms with coverage of 1 ML. As shown in Fig. 6(a), the energy barrier for an adsorbed oxygen atom to diffuse from the hcp (fcc) to the fcc (hcp) hollow site is denoted as $\Delta E_1$ ($\Delta E_2$). The calculated energy barriers for the diffusion of an adsorbed oxygen atom on different Pb(111) films are shown in Fig. 6(b). One can see that $\Delta E_1$ is always smaller than $\Delta E_2$, indicating that the adsorption state at the surface fcc hollow site is more stable than the one at hcp hollow site for all Pb(111) films. The bilayer oscillation behavior can be clearly seen from Fig. 6(b) for the both two kinds of diffusion energy barriers ($\Delta E_1$ and $\Delta E_2$). The beating envelope can also be seen for the 11 ML Pb(111) film. Similar results of being modulated by the QSE of Pb(111) films are also observed for the diffusion of subsurface oxygen atoms. Therefore, we derive that QSE can modulate the diffusion behavior of atomic species on ultrathin metal films.

To investigate the QSE on surface oxidation of Pb(111) films, especially in more detail on the formation of surface oxide layers, we also study the QSE on the penetrations of oxygen atoms after the investigations of the QSE on diffusion energy barriers. It has already been pointed out that the direct penetration for an oxygen atom from the on-surface adsorption site into the tetra-II subsurface site (the site right below a surface Pb atom) without bypassing other subsurface sites is very energetically unfavorable [23]. So we here only consider the penetration of an oxygen atom from the on-surface hcp (fcc) hollow site to the neighboring subsurface tetra-I (octa) site at the coverage of $\Theta = 0.25$.

As shown in Figs. 7(a), the energy barrier for an oxygen atom to penetrate into the subsurface tetra-I site is smaller than the energy barrier for on-surface diffusions. So the adsorbed O atoms are very possible to penetrate into subsurface sites. With the energy bar-
riers for an oxygen atom to penetrate into the subsurface tetra-I and octa sites respectively denoted as $\Delta E_3$ and $\Delta E_4$, one can see from Figs. 7(b) that $\Delta E_3$ is always smaller than $\Delta E_4$ on different Pb(111) films, indicating that the penetration from the on-surface hcp hollow site is always easier. The energy difference between $\Delta E_3$ and $\Delta E_4$ ranges between 0.22 and 0.27 eV for all studied Pb(111) films. As functions of the thicknesses of Pb(111) films, we can see from Figs. 7(b) that the energy barriers for the two penetration paths both show bilayer oscillation behaviors. Therefore, in addition to the modulation on the diffusion energy barriers, the QSE also modulates the penetrations of adsorbed atomic species on metal films.

V. CONCLUSION

In summary, we have systematically studied the adsorption and diffusion energetics of oxygen atoms on different Pb(111) thin films. The surface adsorption energies for atomic oxygen at different coverages have been all found to be modulated by the QSE of Pb(111) thin films. The bilayer oscillation behavior and the 9 ML beating pattern have been identified. After surface adsorption of atomic oxygen, it has been shown that the work function of adsorbed Pb(111) thin films is enlarged, with the same bilayer-oscillation mode as that of the clean Pb(111) thin films. The adsorption energy for subsurface adsorption of oxygen atoms has also been found to be modulate by the QSE and show a bilayer oscillation behavior. Furthermore, we have studied the QSE of Pb(111) thin films on the diffusion and penetrations energetics of adsorbed oxygen atoms, which shows that the most energetically favored diffusion and penetration paths are the same on different Pb(111) films. The corresponding energy barriers have been all found to be modulated by the QSE and display the prominent bilayer oscillations. Therefore, we conclude from our present systematic results that the QSE in ultrathin metal films can modulate a lot of important processes during their surface oxidation.
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Fig.1  (color online) (a) Four on-surface adsorption sites including top, hcp, bri(bridge), and fcc sites. (b), (c) and (d) The tetra-I, tetra-II, and octa subsurface adsorption sites for oxygen atoms. The surface and second layer Pb atoms are shown in black and grey balls, and the oxygen atoms are shown in smaller red balls.

Fig.2  (Color online) Calculated adsorption energy for on-surface O atoms at the fcc hollow site at the 1 ML coverage, as a function of thickness of the Pb(111) films.

Fig.3  (Color online) The adsorption energy for the 0.25 ML on-surface adsorption of oxygen atoms as a function of thickness of Pb(111) films, in comparison with the adsorption energy for the 1 ML adsorption.

Fig.4  (Color online) Work function for clean and O-adsorbed Pb(111) films as a function of the film thicknesses.

Fig.5  (Color online) The adsorption energy for subsurface O atoms at the tetra-II site of Pb(111) films as a function the film thickness.

Fig.6  (Color online) (a) Total energy for an oxygen atom to diffuse on the 13 ML Pb film. (b) Energy barriers for an adsorbed oxygen atom to diffuse on different Pb(111) films as a function of the film thickness.

Fig.7  (Color online) (a) Total energy for an adsorbed oxygen atom on the 13 ML Pb(111) film to penetrate from the on-surface hcp hollow site to the subsurface tetra-I site and from the on-surface fcc hollow site to the subsurface octa site. (b) Calculated energy barriers for an adsorbed oxygen atom to penetrate into the subsurface tetra-I and octa sites, as functions of the film thickness.
FIG. 1:
On-surface adsorption

FIG. 2:
FIG. 3:
FIG. 4:

- **Clean Pb(111) films**
- **After on-surface adsorption**

**Work Function (eV)** vs. **Thickness N (units of ML)**
FIG. 5: Subsurface adsorption
FIG. 6:
FIG. 7: