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Coverage dependence of the work function and charge transfer on the alkali-metal–jellium surface

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The first example of a fully self-consistent electronic structure calculation is presented that elucidates the coverage (Θ) dependence of the work function and the nature of the adatom-substrate bond for alkali-metal overlayers on a jellium surface. The characteristic Θ dependence of the work function observed widely can be reproduced in a straightforward way, without invoking a clustering among adatoms and/or a Θ dependence of the adatom-substrate distance.

Alkali-metal adsorption on metal surfaces has been studied with increasing interest due to its wide variety of electronic properties which are important from both fundamental and technological points of view.[1-5] Among them, the characteristic variation of the work function with coverage Θ has attracted a great deal of attention because of its relevance to cathode technology. The work function first decreases rapidly until it reaches a minimum at about a half-monolayer coverage and then begins to rise toward a saturation value for various combinations of substrate and alkali metal. The work-function change is caused by the adsorbate-induced dipole layer and thus the Θ dependence of the charge redistribution between the alkali-metal adatoms and the substrate is the central object to be disclosed. So far two models have been advanced. In one of them, alkali-metal adatoms are modeled by a uniform jellium slab with a positive background charge density proportional to Θ.[6,7] Though this model is able to reproduce the work-function minimum, its validity is open to question at low coverages where the charge overlap among adatoms is small. The other model, based on the Newns-Anderson-type Hamiltonian, gives a simple physical interpretation of the phenomenon.[8-10] However, the point-charge approximation for the charge transfer adopted in this treatment is crude and it cannot reproduce a work-function minimum comparable to experimental ones without assuming a clustering among adatoms[9] and/or a large relaxation of the adatom-substrate distance with Θ.[10] In any case, these two approaches are phenomenological and therefore a first-principles calculation is indispensable in order to clarify the Θ dependence of the charge redistribution and the nature of chemical bonding between the alkali-metal adatom and substrate.

In the present Rapid Communication, we report the first example of such a calculation. The electronic structure calculations to date for the alkali-metal overlayers[11-13] have been restricted to full coverage because the two-dimensional periodicity of the substrate hinders the continuous change of Θ and also the amount of labor required to perform calculations increases rapidly with decreasing Θ. To resolve mainly the former drawback, we choose jellium as the substrate metal, so that the coverage as well as the structure of the alkali-metal overlayer is at our disposal. Since the observed work-function variation is independent of the detailed character of the substrate, such as the number of d electrons, the choice of jellium as the substrate seems quite acceptable in order to extract the essence of the phenomenon.[10] The results obtained in the present calculation reproduce the observed work-function variation very well. However, the Θ dependence of the charge transfer is quite different from that in the Newns-Anderson model analyses and, thus, part of the simple physical picture accepted so far should be significantly revised.

The calculation is performed within the framework of the local-density-functional theory. We use a plane-wave basis and repeating slab geometry. The nonlocal norm-conserving pseudopotential[14] is employed for the alkali-metal adatom. The distance between the adatom and jellium edge $d(\Theta)$ is determined by total-energy minimization. In the present Communication, we show results for Na overlayers on a jellium surface with $r_s = 2.1$ a.u. This choice of adatom and substrate was previously studied by Lang and Williams[15] as the single-atom chemisorption problem (the limit $\Theta \rightarrow 0$). The Na overlayer is assumed to form a square lattice whose lattice constant $a_\parallel$ is proportional to $\Theta^{-1/2}$. The qualitative aspects of the results do not depend on the structure of the overlayer. For the sake of convenience, we define the atomic density corresponding to $a_\parallel = 8.0$ a.u. as $\Theta = 1$ (values for Θ are in units of monolayers) as it gives a value typical for full coverage. The thickness of the jellium slab is chosen as 16.0 a.u., which can reproduce the work function 3.8 eV of the semi-infinite jellium. The interval between neighboring jellium slabs, 32.0 a.u. is sufficient in evaluating the surface dipole layer to high accuracy. The energy cutoff for the plane-wave basis is 6.5 Ry. With this value, the number of plane waves exceeds 2600 at $\Theta = \frac{1}{3}$, which is near the limit of the present computer capacity. The iteration procedure is continued until the input and output potential difference converges to less than 0.03 eV.

We define the difference charge $\delta\rho(\mathbf{r},\Theta)$ by the equation

$$\delta\rho(\mathbf{r},\Theta) = \rho(\mathbf{r},\Theta) - [\rho_{\mathrm{jel}}(\mathbf{r},\Theta) + \rho_{\mathrm{alk}}(\mathbf{r},\Theta)] \ , \qquad (1)$$

where $\rho(\mathbf{r},\Theta)$, $\rho_{\mathrm{jel}}(\mathbf{r},\Theta)$, and $\rho_{\mathrm{alk}}(\mathbf{r},\Theta)$ denote the electron charge densities of the alkali-metal-overlayer–jellium system, isolated jellium, and unsupported alkali-metal monolayer, respectively. The definition is quite natural in eluci-

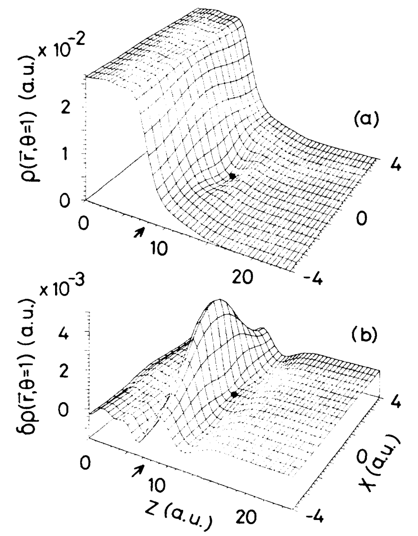

FIG. 1. (a) Electron charge density of the Na-overlayer–jellium surface for $\Theta=1$ in a vertical cut plane passing through Na adatoms at interval of $a_{\parallel}$. The x and z axes are parallel and vertical to the surface, respectively. The jellium edge and the adatom are shown by the arrow and filled circle, respectively. (b) Difference charge density defined by Eq. (1) for $\Theta=1$ in the same plane as in (a).

dating the charge redistribution caused by the interaction between the overlayer and substrate. The work-function change due to the alkali-metal adsorption is obtained from the induced dipole layer by

$$\Delta\Phi(\Theta)=\frac{4\pi}{a_{\parallel}^{2}}\int z\delta\rho(\mathbf{r},\Theta)dr\ . \qquad (2)$$

Dipole moment per one adatom is given by $\Delta\Phi(\Theta)a_{\parallel}^{2}/4\pi$.

The calculation was done for $\Theta=1$, $\frac{3}{4}$, $\frac{1}{2}$, and $\frac{1}{3}$ ($a_{\parallel}=8.0$, 9.24, 11.31, and 13.86 a.u., respectively). Figure 1(a) shows the electron charge density at $\Theta=1$ in a vertical cut plane passing through the Na adatoms at intervals of $a_{\parallel}$. $d(\Theta)$ is determined as 3.1 a.u. from the total energy. Because of the pseudopotential calculation, the charge density is a minimum at the Na sites. The ample magnitude of the charge between neighboring Na atoms indicates that the Na overlayer has a metallic character at this coverage. However, it does not mean that the overlayer is a two-dimensional metal, since the Na valence states strongly hybridize with the jellium bands in the present case. The difference charge at $\Theta=1$ defined by Eq. (1) is depicted in Fig. 1(b). The Θ dependence of the charge redistribution is discussed in detail in the following.

In Fig. 2, we show the contour maps of the difference charge for different Na coverages in the same vertical cut plane as in Fig. 1. The shaded and hatched areas designate the regions where $\delta\rho(\mathbf{r},\Theta)\geq 0.001$ a.u. (accumulation of charge) and $\delta\rho(\mathbf{r},\Theta)\leq -0.0005$ a.u. (depletion of charge), respectively. The charge map for $\Theta=\frac{1}{3}$ bears a close resemblance to that of Li on jellium given by Lang and Williams[15] for single-atom chemisorption. This suggests that direct interaction between adatoms is negligibly small at $\Theta=\frac{1}{3}$. Hence Fig. 2 traces the Θ dependence of the charge transfer in the whole regime during the Na-monolayer formation.

The most striking feature discovered in the present work is that the bond charge is formed between the substrate and adatom irrespective of Θ and that the bond-charge contour (shaded area) and its amplitude are almost unchanged throughout the monolayer formation. Slight expansion (contraction) of the bond-charge contour

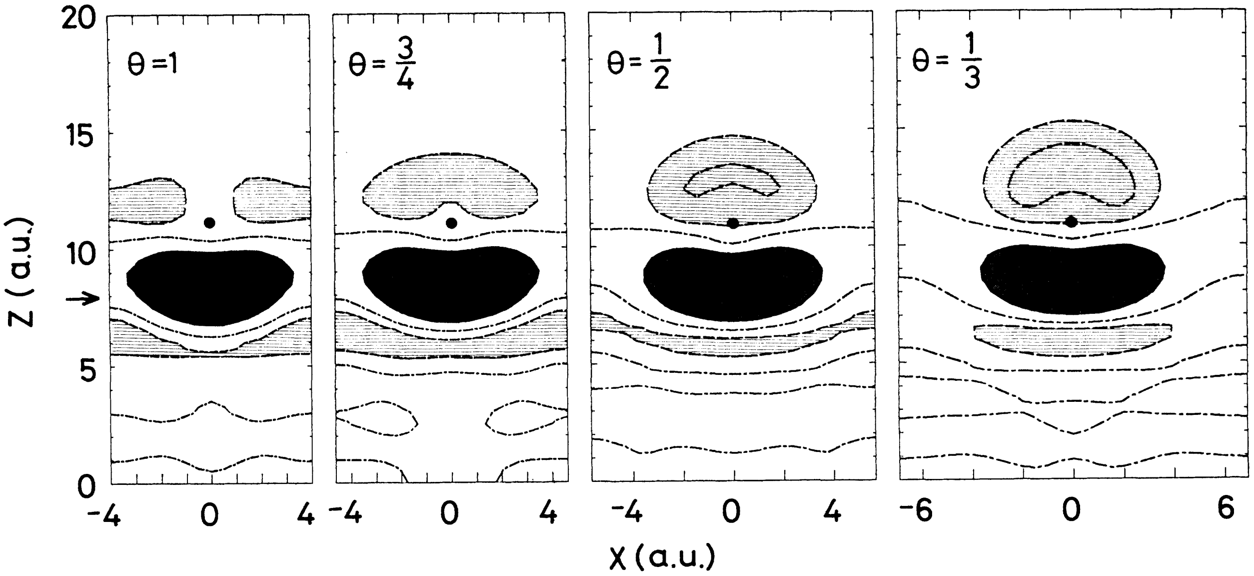

FIG. 2. Contour maps of the difference charge at $\Theta=1$, $\frac{3}{4}$, $\frac{1}{2}$, and $\frac{1}{3}$ (in units of monolayers) in the same vertical cut plane as in Fig. 1. The jellium edge and the Na atom are shown by the arrows and filled circles, respectively. The shaded and hatched areas indicate the regions where $\delta\rho(\mathbf{r},\Theta)\geq 0.001$ a.u. and $\delta\rho(\mathbf{r},\Theta)\leqq -0.0005$ a.u., respectively.

vertical (parallel) to the surface with increasing Θ is the only noticeable minor change. On the other hand, striking Θ dependence exists in the hatched areas from which electrons are transferred into the adatom-substrate bond. At $\Theta = \frac{1}{3}$, most of the bond charge is supplied by the large charge depletion on the vacuum side of a Na adatom, which leads to a large inward dipole moment to reduce the work function. An appreciable amount of ionic character is involved in the adatom-substrate bonding at this coverage. With the increase of Θ, the charge depletion on the Na side decreases, while the resultant deficit in the bond charge is supplemented by electron flow from the jellium substrate. This charge relocation in the substrate induces an outward dipole, which plays an important role in reducing the total inward dipole moment along with suppression of the charge flow from the Na side with increasing Θ. It is seen from Fig. 1(b) that the largest charge loss occurs on the jellium side rather than the Na side at $\Theta = 1$. Another useful comment at $\Theta = 1$ is that the charge depletion on the Na side appears between neighboring Na atoms at the expense of some bonding charge between the Na-Na metallic bond instead of at the outer region of an adatom as at lower coverages.

The above Θ dependence of the charge redistribution is far from the simple picture in the Newns-Anderson-type model analysis. In the model, the charge transfer is described only by one parameter $\Delta n(\Theta)$ and the work-function change is estimated as $\Delta\Phi(\Theta) = 4\pi\Theta d(\Theta) \times \Delta n(\Theta)$.[8-10] It is manifest that the simple treatment cannot take account of the bond charge in the interface region which remains unchanged during monolayer formation and also the charge depletion in the substrate metal. Although the Newns-Anderson model may correctly describe the metallization mechanism of the alkali-metal overlayer, it cannot be applied to a problem where the realistic redistribution of the surface charge density plays a crucial role.

Figure 3 shows the calculated Θ dependence of the dipole moment per one adatom and the work function calculated by Eq. (2). The dipole moment decreases rapidly between $\Theta = \frac{1}{2}$ and $\frac{3}{4}$, which leads to the work-function minimum at about $\Theta = \frac{1}{2}$. The depth of minimum, namely, the work-function difference between $\Theta = 1$ and $\frac{1}{2}$, is comparable to typical experimental values for Na.[3] In the present calculation, the lattice constant $a_{\parallel}$ uniformly shrinks with Θ. Therefore, the clustering among adatoms[9] is not always essential to reproduce the observed work-function minimum.

Here we comment on the role of the $d(\Theta)$ relaxation on the work-function variation recently proposed by Muscat and Batra.[10] In the present calculation, $d(\Theta)$ is determined as 3.1, 3.0, and 2.9 a.u. for $\Theta = 1$, $\frac{3}{4}$, and $\frac{1}{2}$, respectively. We have not yet obtained $d(\Theta)$ for $\Theta = \frac{1}{3}$ because of the long computational time at that coverage and $d(\frac{1}{3}) = 2.9$ a.u. is assumed in Fig. 2. The outward relaxation of the overlayer with increasing Θ is partly due to the decrease of ionicity in the adatom-substrate bond, since the Coulomb attraction energy favors a shorter bond length for ionic bonds. Nevertheless, the change of $d(\Theta)$ of an order of 0.1 a.u., causes the work-function change only of the order of 0.01 eV. Muscat and Batra required a large $d(\Theta)$ relaxation (0.5–1.0 a.u.) for fitting their results to the experimental work-function variation. However, such a value seems somewhat too large even with different choices of substrate and alkali metal, and the disagreement with the experiment may be attributed to their use of a simple model based on the Newns-Anderson Hamiltonian.

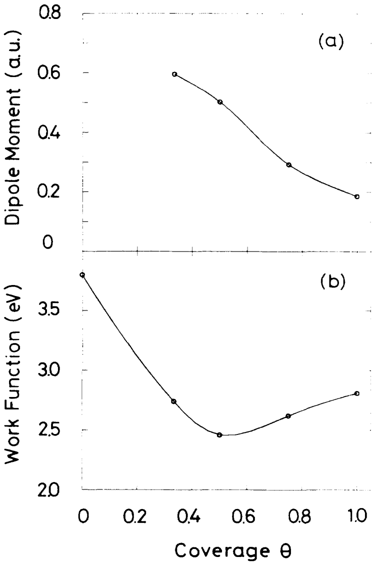

FIG. 3. (a) Calculated coverage dependence (in units of monolayers) of the dipole moment per a Na adatom. (b) Calculated work function as a function of coverage Θ for the Na/jellium surface.

In summary, we have reported the first example of a fully self-consistent electronic structure calculation that elucidates the coverage dependence of the charge redistribution and the nature of the adatom-substrate bonding for the Na-jellium surface. The Θ dependence of the charge redistribution obtained in the present work is physically quite reasonable and seems to be fairly general. The observed work-function variation is reproduced well without invoking a special clustering among adatoms and/or a large $d(\Theta)$ relaxation as far as the spatial redistribution of the charge density is described realistically. The widely accepted simple picture for the Θ dependence of the charge transfer should be thus revised significantly.

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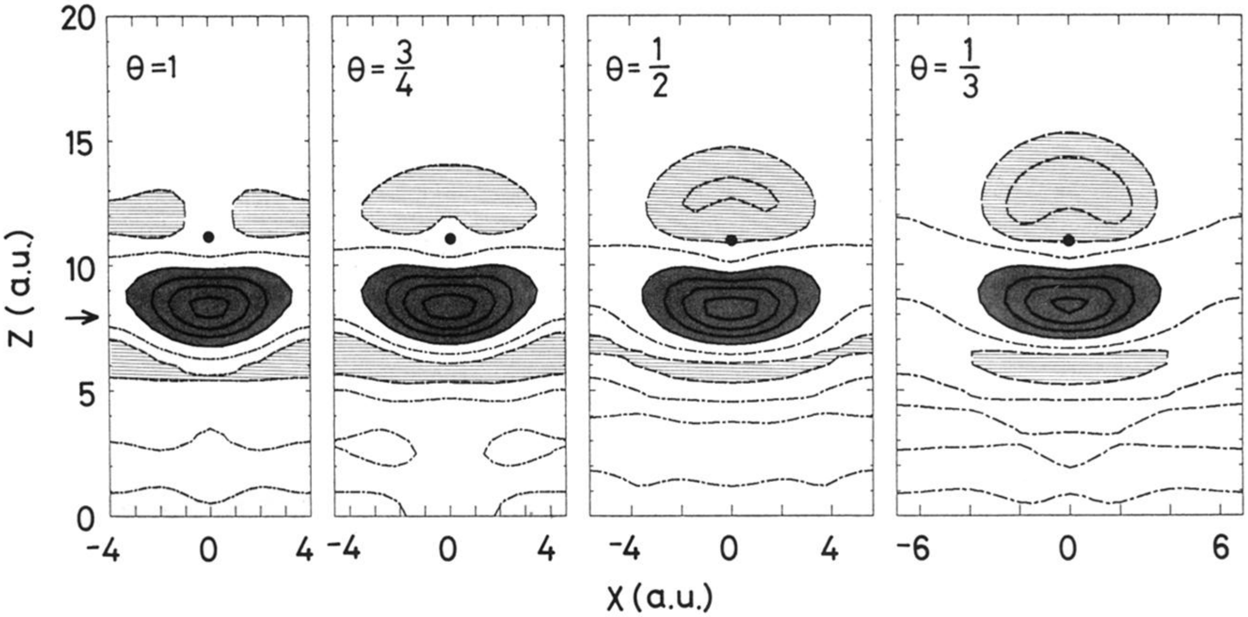

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