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Divide-and-conquer calculations for clean surfaces and surface adsorption

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Abstract. The divide-and-conquer density-functional approach is implemented for electronic structure calculations of clean surfaces and surface adsorption. The method divides a semi-infinite solid-state system into subsystems and determines each subsystem density separately. We have applied the method to study two low index Li surfaces and the chemisorption of a monolayer of atomic hydrogen on the Li(100) surface. Surface and adsorption energies converge well with respect to the number of buffer atoms and surface layers. Our converged energies are in very good agreement with accurate theoretical and available experimental results.

Key words: Density functional theory – Linear scaling – Surface science

1 Introduction

The determination of the electronic structure of clean surfaces and surface adsorption plays an important role in understanding many complicated surface phenomena and catalytic processes [1]. Over the past several decades, a variety of theoretical methods, in particular those based on density-functional theory (DFT) [2, 3], have been developed to complement experimental studies on semi-infinite solid-state systems [4, 5]. These include the slab model [6], the Green's function method [7–9], the local space approximation [10], and various finite-cluster [11, 12] and embedded-cluster methods [13–16]. In the following, we first briefly describe these methods. We then focus on the implementation of the linear-scaling divide-and-conquer method [17] for surface and adsorption.

The most widely used theoretical approach for a semi-infinite solid-state system is to model it by a finite slab with two surfaces separated by several atomic layers of bulk [6]. In the direction perpendicular to surface planes (defined as the z direction here), the slabs are repeated periodically with vacuum in between so that standard three-dimensional band-structure methods can be easily applied to surface and adsorption calculations. Although the slab model can describe surface electronic states reasonably well, there remain some problems in its applications. For reliable results from a slab calculation, the slab has to be thick enough to prevent the interactions between two surfaces and the vacuum has to be large enough to keep adjacent slabs well separated. This usually requires a very large unit cell in the z direction, which presents a challenging problem for first-principles band-structure calculations because of the fast growth of computational expense with increasing system size. In addition, in the slab model the bulk and surface state wavefunctions are not clearly separated, making it difficult to extract surface electronic structures from such calculations. Many other theoretical investigations are based on the first-principles Green's function theory [7–9], which provides an elegant and systematic way for quantum-mechanical studies of surfaces and adsorption on surfaces. The fundamental computational variable in the scattering theory of adsorption is the Green matrix (or equivalently the Kohn-Sham density matrix). The method has been successfully employed for many surface and adsorption calculations [9]. The localized electronic structure of surface and adsorption can also be studied in the local space approximation (LSA) [10] based on Hartree-Fock theory. The simple finite-cluster model is widely adopted in ab initio studies of chemisorption with the use of available computer codes for molecular calculations [5, 11, 12]. Finite-cluster calculations usually provide only a qualitative picture of the electronic structure since the specific values of the electronic interactions, e.g. the adsorption energies, depend significantly on the cluster size. Various embedded-cluster approaches have been proposed to improve the finite-cluster model [5, 13–16]. In an embedding scheme, a finite cluster is embedded in an environment, which is

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usually modeled by point charges or surrounding atoms of the cluster. The potential generated from the environment is included in the cluster Hamiltonian, and the electronic structure for the embedded cluster is then determined. Embedded-cluster methods have been successfully applied to many studies of clean and reconstructed surfaces, adsorption, and chemical reactions on surfaces [5]. However, in most embedded-cluster calculations, total energies converge very slowly with respect to the cluster size. This problem is mainly due to the lack of a rigorous treatment for complex boundary effects and for charge transfer between the cluster and the environment. In all these methods for extended systems, the computational effort scales at least as cube of the number of atoms involved in the region of interest.

In recent years, a number of linear-scaling ab initio methods have been proposed for electronic structure calculations of large systems [17–32]. The divide-and-conquer density-functional approach of Yang first demonstrated the possibility [17]. In the divide-and-conquer method, a large system is divided into subsystems and each subsystem density is determined separately from the solution of a local Hamiltonian matrix equation. The total electron density is the sum of all subsystem contributions. The N^3 scaling of the Kohn-Sham (KS) scheme is eliminated in the divide-and-conquer approach because it does not require the construction and diagonalization of a matrix for the entire system. The method has been tested extensively and is shown to be as accurate as the KS scheme [33, 34]. A density-matrix version of the divide-and-conquer method has also been proposed, making the method applicable to Hartree-Fock and semiempirical calculations [35]. We have recently implemented the method to calculate cohesive and structural properties of crystalline solids without involving band structure [36].

Since the divide-and-conquer method [17] is a real space approach like the Green's function method [9], it is suitable for calculations of semi-infinite solid-state systems, where translational symmetry in the z direction is broken. We can divide a semi-infinite solid-state system into subsystems and calculate explicitly the electron densities of those subsystems of interest. In this sense the divide-and-conquer method can be considered as an embedded-cluster approach. In the "divide-and-conquer embedding", both the embedded cluster and the environment are treated as subsystems. The one-electron effective potential, which enters the local Hamiltonian for each subsystem, includes contributions from the entire semi-infinite system. The boundary effects are treated in a systematic fashion with the inclusion of contributions from more and more buffer atoms (neighboring atoms) for each subsystem [33]. The charge transfer between the region of interest and the environment is effected by chemical potential equalization. In this letter, we first present the implementation of the the divide-and-conquer method for clean surface and periodic adsorption calculations. We then provide the results from the divide-and-conquer calculations for clean Li(100), Li(110) surfaces, and the interaction of a monolayer atomic hydrogen with the Li(100) surface.

2 Implementation

The current computational implementation of the divide-and-conquer method for semi-infinite systems follows that for bulk solids in our earlier work [36]. We only address the points of difference here. We have chosen a more realistic theoretical model than a slab. We treat the several atomic layers closest to the vacuum as surface layers and treat the rest of the system as bulk. The surface layers have two-dimensional periodicity (in the $x - y$ plane) and can be constructed from one surface unit cell. To carry out the divide-and-conquer calculations, we first partition the surface layers into surface unit cells and divide each cell into subsystems. We then determine the buffer atoms for each subsystem in the representative surface unit cell according to their distances from the subsystem. Note that buffer atoms constructed in this way include not only the atoms in the surface layers but also atoms from the bulk. We calculate the total electron density within one surface unit cell by explicitly determining the subsystem densities. The electrostatic potential is computed in a similar way as in divide-and-conquer calculations for bulk solids [36]. The deformation potential is partitioned into a short-range part and a long-range part. The short-range part is obtained from the solution of the Poisson equation based on Delley's method [37]. We only need to perform projections to obtain the multipolar components of the deformation potential for those symmetry-independent atoms in the surface layers. The corresponding values for bulk atoms are taken from our previous bulk calculations. The long-range part is computed by the surface Ewald technique developed by Parry [38]. We have calculated the deformation charges for each atom in the central surface unit cell and used them in the surface Ewald formula to obtain the long-range electrostatic potential. To find the proper chemical potential in our calculations, we assume that there is no charge transfer along the z direction if a sufficient number of surface layers are used. This means that we use the number of electrons in the central surface unit cell for the density normalization. Our test calculations on Li surfaces and H/Li(100) indicate this approach works quite well.

3 Results and discussion

3.1 Lithium surfaces

Clean Li(100) and Li(110) surfaces have been studied by a number of theoretical calculations [39, 40] and experimental techniques [41, 42]. They provide a good test for our implementation mainly because accurate surface energy data are available for these two surfaces. In our calculations, we select a number of atomic layers close to vacuum to be the surface layers to model the Li surfaces and divide the surface layers into equivalent surface unit cells. For simplicity, we consider each surface unit cell as a subsystem. For each subsystem, buffer atoms are selected from the neighboring atoms according to their distances from the atoms in the

Table 1. Number of buffer atoms and surface energies of the clean Li(100) and Li(110) surfaces in divide-and-conquer calculations that use different buffer schemes (B_m) and number of surface layers (L_n). The P basis set (3s/1p) is used. Experimental values [40] and other theoretical results [40] are listed for comparison

	Buffer atom			Surface energy (eV)					
	B_2	B_3	B_4	B_2	B_3	B_4	Jellium	Green's function	Expt.
Li(100)									
L_2	29	52	78	0.35	0.43	0.38			
L_3	38	65	96	0.27	0.37	0.32			
L_4	47	78	114	0.32	0.39	0.32	0.28	0.33	
Li(110)									
L_2	31	57	85	0.22	0.30	0.24			
L_3	42	75	110	0.19	0.29	0.23			
L_4	53	93	135	0.17	0.29	0.25	0.22	0.25	0.33

subsystem to form a set of buffer clusters. Each buffer cluster corresponds to a buffer scheme (Table 1). The experimental lattice constant of 3.491 Å is used in all calculations (no surface relaxation is considered). The cutoff radius for the short-range summation [36] in the calculation of the electrostatic potential is chosen as 20 a.u. About 3,000 integration points per atom are used to achieve the integration accuracy of 10^{-5} a.u. in density and electrostatic energy. Numerical basis sets are the same as those in bulk Li calculations [36]. For the local-density approximation (LDA), the Vosko-Wilk-Nusair (VWN) [43] parametrization is used.

We have performed LDA total-energy calculations for Li(100) and Li(110) surfaces using the P basis set [36]. We have varied the number of surface layers and the number of buffer atoms to test the energy convergence. The surface energy, which is the work required to form a unit area of surface, is computed as follows:

$$E_{\text{surf}} = E_n - nE_{\text{bulk}}, \tag{1}$$

where E_n is the total energy per surface unit cell with n atoms from the divide-and-conquer calculations, and E_{bulk} is the energy per atom of bulk lithium. The calculated surface energies for the Li(100) and Li(110) surfaces are summarized in Table 1.

We observe the following from the two parts of Table 1: (a) If the number of surface layers is fixed, the surface energy usually converges to around 0.1 eV when about 40–60 buffer atoms are used in the calculations. This is similar to the energy convergence behavior in the divide-and-conquer calculations for molecules and bulk solids. (b) If enough buffer atoms are used, the surface energy converges fast with respect to the number of surface layers (calculations with only two surface layers already converge surface energies to less than 0.1 eV). (c) Our computed surface energies for Li(100) and Li(110) surfaces agree very well with the results from the jellium model calculations [39], the self-consistent Green's function calculations [40], and the experimental values [41, 42]. These results show that our implementation of the divide-and-conquer approach for surface calculations is successful. We expect the present work can be extended to the ab initio calculations of more complex surface systems.

3.2 Atomic hydrogen on Li(100) surface

The chemisorption of atomic hydrogen on a clean Li(100) surface has attracted great interest in recent years despite the present scarcity of experimental data. There are two main reasons for theoretical investigations on this system. First, H/Li(100) is generally considered as the prototype for the interaction of atomic hydrogen with metal surfaces. Second, the system is relatively simple so extensive ab initio calculations can be carried out. Many theoretical investigations are based on cluster-type models, either with finite size or with embedding environment. The first ab initio study of this system was made by Beckmann and Koutecky using a multireference double-excitation configuration-interaction approach [44]. Later, Hira and Ray utilized the Hartree-Fock method and many-body perturbation theory to perform a series of calculations on Li clusters interacting with atomic hydrogen [45]. These calculations show the computed adsorption energies and geometries strongly depend on the cluster size and shape, making it difficult to derive conclusive results. Ravenek and Geurts implemented Pisani's moderately large-embedded-cluster (MLEC) scheme and applied it to the on- top adsorption of H/Li(100) using the pseudopotential Hartree-Fock-Slater method [46]. Unfortunately, no data concerning adsorption geometry and energetics were reported in their paper. Krüger and Rösch also implemented the MLEC scheme in LDA calculations of the H/Li(100) chemisorption [47]. Optimized adsorption geometries, adsorption energies and other electronic properties from both free-cluster and embedded-cluster calculations were presented. There are significant fluctuations of calculated properties with different cluster sizes even when embedding is utilized. Recently, Casassa and Pisani have undertaken a Hartree-Fock perturbed-cluster study on H/Li(100) and found appreciable adsorption energy (60–80 kcal/mol) [48]. Other theoretical investigations have considered periodic hydrogen overlayers on top of thin films or slabs of Li atoms. Flores and co-workers used a model Hamiltonian based on the parametrization of Hartree-Fock results to study the adsorption of a monolayer of H on top of a fourfold hollow site of Li(100) surface [49]. Casassa and Pisani also reported some results for H/Li(100) from periodic Hartree-Fock calculations [48]. Detailed LDA band-structure calculations have been carried out by Rösch et al. to provide more physical and chemical insight into the chemisorption process of H/Li(100) [50].

We have performed the divide-and-conquer calculations to investigate the interaction of a monolayer of atomic hydrogen with the clean Li(100) surface. We only consider the on-top adsorption site since the main purpose here is to test our implementation. For simplicity, we take the hydrogen concentration as 1:1, i.e. one surface Li atom corresponds to one H atom. The distance between the H atom and the Li(100) surface is

Table 2. Number of buffer atoms and adsorption energies of a monolayer of atomic hydrogen at the on-top site of a clean Li(100) surface from the divide-and-conquer calculations that use different buffer schemes (B_m) and number of surface layers (L_n). The H-Li(100) distance is 1.7Å. The P basis set (3s/1p) is used. The MLEC result is taken from Ref. [47]

	Buffer atom				Adsorption energy (eV)				
	B_1	B_2	B_3	B_4	B_1	B_2	B_3	B_4	MLEC
L_2	22	38	61	72	−1.08	−1.00	−0.97	−0.99	
L_3	28	47	74	87	−1.08	−0.99	−0.90	−0.90	
L_4	34	56	87	102	−1.14	−1.00	−0.90	−0.91	−0.86, −1.52

chosen as 1.7Å. This is the optimized value from the previous LDA calculations based on the MLEC scheme [47]. The buffer schemes are listed in Table 2. The adsorption energy is computed as

$$E_{\text{ads}} = E_c - E_s - E_H, \tag{2}$$

where E_c is the total energy per unit cell of H/Li(100), E_s is the total energy per surface unit cell of the Li(100) surface and E_H is the spin-polarized energy of atomic hydrogen. In Table 2, we present the adsorption energies obtained from calculations that use different number of Li surface layers and buffer atoms.

It is very encouraging to see from Table 2 that the calculated adsorption energies converge well with respect to the number of surface Li layers and the number of buffer atoms. The largest difference among the reported adsorption energies is only 0.2 eV. Our converged adsorption energy is also close to the values from the LDA MLEC calculations with embedded clusters of 14 and 18 Li atoms [47]. In these calculations, the adsorption of a single atomic hydrogen on Li(100) surface is studied. As shown by Birkenheuer and co-workers in their LDA slab calculations, both the adsorption energy and the equilibrium distance of H/Li(100) scarely depend on the hydrogen concentration [50]. Therefore, we consider the comparison between our results and those from the MLEC calculations [47] a valid one.

In our scheme for the calculation of the electrostatic potential, the deformation density is decomposed into atomic contributions [36]. With this decomposition, the net charge on each atom can be easily defined as

$$Q_A = -\int \rho_A^{\text{def}}(\vec{r} - \vec{R}_A)\,\mathrm{d}\vec{r}, \tag{3}$$

where $\rho_A^{\text{def}}(\vec{r} - \vec{R}_A)$ is the multipolar component of the deformation density on atom A. In our calculations, we have observed that charge transfer mainly occurs between the adsorbed hydrogen atoms and the first layer of Li atoms, with the top Li layer positively charged. For example, in the largest calculation we have performed on H/Li(100) with the use of 102 buffer atoms and four surface layers, the net atomic charges on the H atom and Li atoms (starting from top surface layer) are −0.098, 0.091, 0.027, −0.014, and −0.006 respectively. The magnitude of charge transfer is smaller for Li layers deeper into the bulk. This agrees with a number of theoretical investigations [46–48].

4 Summary

We have extended the divide-and-conquer approach for first-principles calculations of clean surfaces and periodic adsorption structures on surfaces. Test calculations on two low index Li surfaces and the adsorption of a monolayer of atomic hydrogen on the Li(100) surface have shown very promising results. Surface and adsorption energies from our divide-and-conquer calculations normally converge to 0.1 eV when 40–60 buffer atoms are included. The energies converge rapidly with respect to the number of surface layers (only two or three surface layers are needed to reduce the errors in energies to less than 0.1 eV). The connection between the surface region and the bulk can be better represented by including more buffer atoms from the bulk. We expect the method to be useful to study more complex chemisorption problems, such as the adsorption of small organic molecules on transition metal surfaces.

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