PHYSICAL REVIEW B **79**, 045403 (2009)

Potential-energy surfaces of adsorbates on periodic substrates: Application of the Morse theory

Štěpán Pick*
J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i.,
Dolejškova 3, CZ-182 23 Prague 8, Czech Republic

(Received 24 October 2008; revised manuscript received 12 December 2008; published 7 January 2009)

We employ the Morse theory of critical points (extrema and saddle points) of functions on compact manifolds to analyze the potential-energy surface of adsorbates on periodic crystalline surfaces. Formulation of the theory for this case is very simple and allows one, e.g., to check completeness or consistency of a proposed potential-energy surface topology. For highly symmetric adsorption or surface-diffusion systems and/or when some additional information on the potential energy is available, the theory can be predictive. For example, if the most stable adsorption position for a symmetric adsorbate is the bridge site on bcc or fcc(001) surfaces, or on fcc(111) and hcp(0001) ones, the saddle points of the potential energy will appear away from top and hollow sites. Application of the Morse theory is illustrated on examples of known adsorption systems.

DOI: 10.1103/PhysRevB.79.045403 PACS number(s): 68.43.Fg, 68.43.Jk, 02.40.Sf

I. INTRODUCTION

Determination of the diffusion path(s) of molecular or atomic adsorbates on solid crystalline surfaces is of crucial importance in catalysis.[1–3] The key feature is the clarification of basic properties of the adsorbate potential-energy surface (PES) as a function of its position above the surface. The same potential surface can be helpful in the determination of the stable adsorption sites and the geometry of adatom overlayers.

It might seem that a formal mathematical analysis is restricted essentially to applications of the group theory. Recently, however, an extension of the theory for complicated surface structures has been formulated.[4] In the present paper we show that by employing the surface periodicity, one can obtain useful information on the possible number of critical points on the PES (local minima and maxima and saddle points) and on the relation between the number of critical points of particular kinds. To this goal, the mathematical theory of Morse[5–7] of functions on compact manifolds is used. Although the Morse theory represents a specific chapter in algebraic topology, the results we need represent only a fraction of this theory and can be formulated as a rule of thumb. With their aid one can prove that a list of critical points obtained in calculations is not complete or, on the contrary, is most probably complete, and some inconsistency in PES models can be traced. For systems possessing a higher symmetry, especially when, e.g., the most stable adsorbate position is known, the theory is yet more predictive. Let us note that an application of the Morse theory to the PES of small molecules (residing in vacuum) has been undertaken in chemistry.[8,9]

All mathematical facts that we are going to mention can be found in mathematical textbooks, some of which are listed in the reference section at the end of the paper. However, since the reader may not be familiar with some notions and results, we gather them also in Sec. II. Instead of adopting the fully rigorous approach, we explain part of the material on the simple case of the two-dimensional (2D) torus. After that, the application of the mathematical theory is explained and illustrated on examples of well-known chemisorption systems that are taken from the literature.

II. METHODOLOGY

Let us consider a crystalline surface possessing a 2D periodicity defined by two elementary-translation vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ that generate a discrete symmetry group of translations G. Points on the surface are described by a 2D vector $\mathbf{R}$ when an appropriate coordinate system is fixed. Let us denote as $E(\mathbf{R})$ the potential energy of an adatom above the surface as a function of $\mathbf{R}$. Often, valuable information (as a rule, the most stable adatom positions) is provided by experiments. In calculations, it is supposed that for a given $\mathbf{R}$, all or certain selected from the remaining degrees of freedom (height of adatom above the surface, lattice deformation due to the adatom presence, magnetization, etc.) are allowed to relax, be it in calculations or in a gedanken experiment. The same idea applies to molecular adsorption, coadsorption of several atoms, or infinite adsorbate overlayers, with $\mathbf{R}$ being now a position of a selected atom, whereas positions of other atoms in the system are allowed to relax as $\mathbf{R}$ varies. Let us stress that we are always working within the surface (1×1) elementary cell, treating the overlayers with a higher $(m \times n)$ periodicity as large molecules. Clearly, we obtain in this way $E(\mathbf{R})$ as a doubly periodic function with two periods $\mathbf{t}_1$ and $\mathbf{t}_2$. It is convenient to consider $E(\mathbf{R})$ as a function on the 2D torus T^2 (Fig. 1) that is obtained from the plane representing the crystal surface by identifying points that are

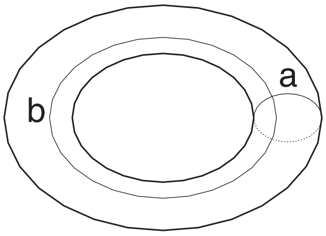

FIG. 1. The two-dimensional torus T^2. See Sec. II for a description of the loops **a** and **b**.

equivalent with respect to the group G. (More formally, T^2 is the quotient space R^2/G, where R^2 is the 2D plane.) The reader interested in applications to surface science only can skip the rest of this section.

The tirelike surface T^2 provides a simple example of a *connected compact manifold*. Obviously (under "common" regularity assumptions), PES attains on T^2 its absolute maximum and absolute minimum (the most stable position of the adsorbate) at certain points. A mathematical theory we owe to Morse[5–7] for functions on similar manifolds states much more as the number of local minima, maxima, and saddle points and some relation among them are concerned. The Morse results are formulated by using the notion of *Betti numbers* (rank of homology groups). For our purposes, it is most convenient to give highly simplified definitions and then explain these somewhat abstract ideas of algebraic topology on the example of T^2.

We shall consider the class of real smooth *Morse functions* on an nD (connected and compact) manifold M^n. A Morse function F has *critical points* (points on M^n where grad $F=0$) in isolated points only. Besides that, it is supposed that the matrix of second derivatives of F (Hessian) has the maximal rank n in critical points. The main reason for the restriction on the Hessian is to avoid situations when on the one-dimensional (1D) cross section of a PES by a coordinate plane, a critical point represents an inflection point. Let us place the critical point to the coordinate origin and consider F along a selected coordinate x. Near $x=0$ we have $F(x)=ax+bx^3+\cdots$. For nonzero $|a|\ll|b|$ the critical point disappears ($ab>0$) or we find two close extrema ($ab<0$) that degenerate into a single inflection point at $x=0$ as a vanishes. The function $bx^3+\cdots$ is monotonous and does not represent any special interest. This example reflects a general situation: for a smooth function of n variables, the non-Morse character (degenerate Hessian) of isolated critical points is unstable with respect to arbitrarily small perturbations.[10] It is the idea of the *catastrophe theory*[10] that non-Morse critical points in real systems appear only when they are fixed by tuning a continuous parameter (e.g., temperature) and can signalize a change in the regime (bifurcation and phase transition) of the system. This opinion is shared by specialists[11] on PESs in chemistry as well. In another words, we expect that for realistic potential surfaces the violation of the assumption on the Hessian is an unlikely degenerate case unless there is a physical reason for such a degeneracy. The critical points of Morse functions represent "true" extrema or saddle points, and we shall suppose below that the PESs we study here belong with the Morse functions. We need yet a simple definition. *Index* $i(F,p)$ of F at a critical point $p\in M^n$ is equal to the number of *negative* eigenvalues of the corresponding Hessian. Clearly, one has a maximum of F for $i(F,p)=n$ and a minimum for $i(F,p)=0$. We shall denote as $\mu_k(F)$ the number of critical points of F with the index equal to k. In Sec. III, the simplified notation μ_k will be used when applied to the PES $E(\mathbf{R})$.

Let us sketch now very briefly the definition of Betti numbers. It is understood that all constructions we are going to describe are done "within" M^n. A "regular" kD figure ($k=0,1,\ldots,n$) is called *k cycle* if its boundary is the empty set. A k cycle is *trivial* if it is itself a boundary of a $(k+1)$D figure. Indeed, it can be shown that the "boundary has no boundary" and so trivial cycles have no relation to the properties of M^n. Two k cycles that can be deformed continuously one into another and/or differ by a trivial cycle are considered as mutually equivalent. It appears that for every k there exists a finite number of classes of nonequivalent, nontrivial k cycles that serve as a basis. Any k cycle can be constructed by combining cycles from these classes, maybe up to a trivial k cycle. (The classes are generators of the kth homology group; the class of trivial k cycles is the neutral element in the group. To describe the construction properly, one should also discuss the *orientation* of cycles.) The number of these bases classes is[6,12] the kth Betti number $b_k(M^n)$. The best way to explain the notion is to consider the torus T^2 in Fig. 1. For $k=0$ or 2, the only nontrivial class is represented by a single point on T^2 and by T^2 itself, respectively. (For M^n, $b_0=b_n=1$ for the same reason.)

For $k=1$, there are two independent classes represented by the loops **a** and **b** in Fig. 1 and $b_1(T^2)=2$. For the 2D sphere S^2, $b_1=0$ since every loop on the sphere is a boundary of an area. We are now prepared to write down the theorems[5,6,8,9] relating some properties of critical points to the Betti numbers.

Morse inequalities. For a Morse function F (using the notation introduced above) the following inequalities hold true:

$$\mu_k(F)\geq b_k(M^n),\quad k=0,1,\ldots,n. \tag{1}$$

Relation to the Euler-Poincaré characteristic. By introducing the Euler-Poincaré characteristic $\chi(M^n)=\Sigma_{k=0}^{n}(-1)^k b_k(M^n)$ of the manifold, one has the relation

$$\sum_{k=0}^{n}(-1)^k\mu_k(F)=\chi(M^n). \tag{2}$$

For manifolds we have met, $\chi(T^2)=0$, $\chi(S^2)=2$. Formula (2) can remind the reader of the famous *Euler's formula* $v-e+f=2$ valid for convex polyhedra (v, e, and f are the number of vortices, edges, and faces of the polyhedron). Actually, the formula admits generalization[12] with the Euler-Poincaré characteristic on the right-hand side (2 is the value for the sphere S^2 into which the polyhedron surface can be deformed). It is amazing that this can be done using quite elementary mathematical means only.[13] We mention yet the inequality

$$\begin{aligned}&\mu_k(F)-\mu_{k-1}(F)+\cdots+(-1)^k\mu_0(F)\\&\quad\geq b_k(M^n)-b_{k-1}(M^n)+\cdots+(-1)^k b_0(M^n),\\&\quad k=0,\ldots,n-1.\end{aligned} \tag{3}$$

[By inserting $-F$ into Eq. (3), some new inequalities can be obtained.]

It will be useful to show a method to evaluate Betti numbers for topological products of manifolds. Let us associate with a mD manifold X the *Poincaré polynomial* $P_X(t)=\Sigma_{k=0}^{m}b_k(X)t^k$. According to Ref. 14, for the product $X\times Y$ of two manifolds one can write (this result also easily follows from theorems for homology groups of topological products given in Ref. 6)

$$P_{X\times Y}(t) = P_X(t) \cdot P_Y(t). \quad (4)$$

Let us note also the useful relation

$$P_X(-1) = \chi(X). \quad (5)$$

To close this section, let us mention other potential applications of the Morse theory. For diffusion in three-dimensional (3D) periodic crystals, one needs to consider the 3D torus $T^3 = S^1 \times S^1 \times S^1$, where S^1 is the 1D sphere (circle circumference). It is easy to derive topological characteristics for the nD torus T^n (product of nS^1) by using Eqs. (4) and (5); since its Poincaré polynomial is $(1+x)^n$, we get $b_k(T^n) = \binom{n}{k}$ and $\chi(T^n)=0$. (Since the interaction becomes divergent as the diffusing particle approaches a lattice atom, one has to suppose a regular maximum in this point during the analysis.) Another system that we mention is a physical system with n inequivalent magnetic moments. In this case, the number of spins and not the dimension of the system is the relevant parameter. Let us consider the energy as a function of magnetic-moment orientation. Actually, periodicity of the atomic arrangement is not important here; it is irrelevant whether the atoms belong to an elementary cell in a periodic structure or to an atomic cluster. The controlling parameter for each magnetic moment is its direction in the space, i.e., position on the 2D sphere S^2, and the manifold we need to construct is a product of n spheres S^2. By considering the Poincaré polynomial $(1+x^2)^n$, we arrive at the Betti-number values $b_{2k} = \binom{n}{k}$, $b_{2k+1}=0$, and $\chi = 2^n$ for this structure.

III. DISCUSSION AND EXAMPLES

Equations (1) and (2) are quite general and they can be used, for example, to verify whether some critical point(s) on the PES is not missing in the set obtained in calculations. We shall show, however, that the use of these equations can easily rationalize properties of frequently met symmetric adsorbate patterns. On high-symmetry crystal surfaces such as bcc or fcc(001), fcc(111) and hcp(0001), and fcc(110), certain sites can be considered as candidates for adsorption because of their high symmetry. Indeed, by supposing that their symmetry is not spoiled by the adsorbate, the symmetry guarantees that grad $E(\mathbf{R})=0$. The symmetry is not broken by atomic adsorbates, but this property is conserved also for some simple molecular adsorbates indeed. For example, for CO on late transition-metal surfaces the calculations confirm that the molecule adsorbs upright (or almost upright) in high-symmetry points[2,15] and the latter thus represent critical points of the PES. Analogous behavior can be perhaps anticipated also for other small symmetric molecules such as NO or NH_3. Let us now remind the reader of these highest-symmetry surface sites.[16,17] There are the threefold and fourfold *hollow* (also center) sites that are quite often preferred by atomic adsorbates. Actually, one has to discriminate between the threefold fcc and hollow hcp sites depending on their position with respect to the subsurface substrate layer. Adsorption energies at these two sites are often rather similar. Further, there is the *bridge* site and the least coordinated *top* (or peak) position. At anisotropic surfaces [(110)fcc] there are nonequivalent *short-bridge* and *long-bridge* sites, respectively, with generally rather different bonding capacity. It is interesting that for CO adsorption at low coverage on transition-metal faces, all three adsorption sites, top, bridge, and hollow, are experimentally observed or theoretically predicted.[15,18,19] The investigation of CO adsorption is a delicate task because of the tendency of the commonly used density-functional schemes to overestimate stability of the highly coordinated adsorption sites, and corrections should be applied in the calculations.[18,19]

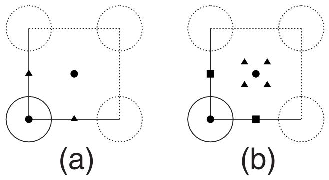

FIG. 2. The elementary cell on the bcc or fcc(001) crystal surface. Open circles represent the surface atoms. The surface atoms and lines that are drawn by dotted lines coincide with their counterparts drawn in full line on the torus T^2 (see text). (a) and (b) show the simplest and the second simplest structures of the potential-energy surface, respectively. Black dots denote extrema positions and black triangles denote positions of saddle points on the potential-energy surface in part (a). In (b) we distinguish between minima (black squares) and maxima (black dots).

We shall consider below the adsorption of an isolated adsorbate or an ordered overlayer with adsorbates occupying equivalent sites on the substrate surface. It is useful to present first Eq. (2) in the form applicable to the torus T^2,

$$\mu_0 - \mu_1 + \mu_2 = 0. \quad (6)$$

μ_0, μ_1, and μ_2 are the number of local minima, saddle points, and local maxima on the PES, respectively. The most important consequence of Eq. (1) is

$$\mu_1 \geq 2, \quad (7)$$

whereas taking $k=1$ in Eq. (3) (and also utilizing the remark following it) we get

$$\mu_1 - \mu_0 \geq 1, \quad \mu_1 - \mu_2 \geq 1. \quad (8)$$

As the most simple case, let us consider the situation when the number of extrema on the PES is the minimal possible one by respecting simultaneously the fact that the symmetry sites listed above are critical points. For the bcc or fcc(001) and for fcc(111) or hcp(0001) surfaces we get the situation depicted in Fig. 2(a) (two extrema and two saddle points, i.e., $\mu_0 = \mu_2 = 1$, $\mu_1 = 2$) and Fig. 3(a) (three extrema and three saddle points, i.e., $\mu_0 + \mu_2 = 3$, $\mu_1 = 3$). [The two extrema in hollow sites in Fig. 3 are generally not equivalent; see the remark above. Besides that, the symmetry of the bridge sites

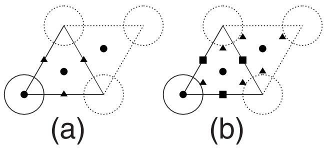

FIG. 3. The same as in Fig. 2 for the elementary cell of the (111) surface of an fcc crystal or (0001) surface of an hcp crystal.

is only C_v because of the above nonequivalence of hollow sites. When interaction of the adsorbate with the more distant subsurface metal atoms is neglected, the symmetry of the bridge site is higher: C_{2v}. Hence, the adsorption site can appear slightly perpendicularly shifted from the center of the bridge (not shown in the figure).] Very often, the atomic adsorbates prefer the hollow sites (cf., e.g., Refs. 17 and 20) that become thus minima on the PES. From the Morse theory it follows that in this simple case, the bridge sites *must* be saddle points. The bcc(110) surface layer can be regarded as a deformed structure shown in Fig. 3, in which the horizontal bridge site is changed in the long-bridge (or hollow) one. On this surface, the quasithreefold site (that actually has symmetry not high enough to imply grad $E=0$) is the stable adsorbate position[16] for oxygen in the $p(2\times2)$O/W(110) system. Up to the deformations just described, the PES topology of this system is consistent with Fig. 3(a).

We have just proven that for the simplest PES the bridge adsorption positions cannot be extrema on the PES. Yet experiments and calculations show[15,17,18] that for some transition-metal surfaces, CO prefers just this geometry. The possible PES topology is shown in Fig. 2(b) ($\mu_0=2$, $\mu_1=4$, $\mu_2=2$) and Fig. 3(b) ($\mu_0=3$, $\mu_1=6$, $\mu_2=3$). Let us stress that there *must* appear saddle points in "unexpected" positions to satisfy Eqs. (6) and (8). They are situated, nevertheless, at symmetry directions in the elementary cell. If they lay in general points at the PES, the C_{4v} or C_{3v} symmetry would enlarge their number, forcing simultaneously existence of a higher number of extrema according to Eq. (6) and the PES would become very complicated. [Structures with other minima and maxima distributions are also consistent with the Morse theory by supposing that the sum $\mu_0+\mu_2$ does not change. Besides that, the quadruples of saddle points in Fig. 2(b) [triples in Fig. 3(b)] can be rotated by 45° (by 60°).] Good news from the analysis of Figs. 2 and 3 is that when seeking for the stable adsorption sites on corresponding surfaces, it is sufficient to do the calculations for the highest-symmetry sites.

It is instructive to compare Fig. 2 with the results of the calculation of Eichler and Hafner[2] for CO adsorption at Pd(001), performed to gain better insight into numerous experimental studies for this system. They confirmed the bridge site as the stable adsorption position. They found an activation barrier for the CO transition between the hollow and bridge sites, respectively, which conforms to the position of saddle points in Fig. 2(b). On the other hand, the calculations do not discover any barrier for the transition between the top and bridge sites, although in experiments[21,22] the top sites behave as metastable ones. The authors discussed[2] the possibility of missing another saddle point in the calculation. Actually, it follows from the Morse theory that appearance of such new points would be associated inevitably with the existence of other extrema that would make the PES unlikely complicated. The authors offered another explanation:[2] the energetically favorable channel for the escape of CO from the top position is very narrow which hinders the transition. Another reason might be the necessity of correlated displacements of CO at a higher coverage[22] that also hinders the transitions. The PES structure in Fig. 2 is also consistent with the density-functional derived models of oxygen adsorption at dereconstructed Pt(001) and Ir(001) surfaces[23,24] [see also Ref. 25 for a Pt monolayer at the Fe(001) substrate].

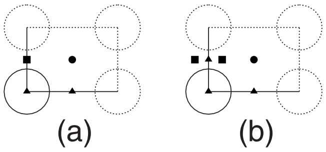

FIG. 4. Structure of the PES for CO adsorption on Pd(110) (see text). The meaning of the symbols is the same as in Fig. 2.

Another interesting example is oxygen adsorption at the anisotropic Pd(110) surface. The theoretical investigation of the PES (Ref. 1) places the stable adsorption site to the quasi-short-bridge position (a position slightly shifted from the short-bridge one). Since according to the calculations[1] the adsorption energy further drops in the sequence long-bridge–hollow site, we can suggest the PES topology shown in Fig. 4(b). Clearly, $\mu_0=2$, $\mu_1=3$, and $\mu_2=1$. At low oxygen coverage the stable adsorption site might be perhaps[1] the short-bridge site. This leads to a more simple Fig. 4(a) with $\mu_0=1$, $\mu_1=2$, and $\mu_2=1$.

Naturally, application of the Morse theory to more complicated situations would be desirable. As a possible example, let us mention the nondissociative adsorption of the oxygen molecule at Pt(111). For this system, a number of calculated data for selected paths on the PES have been published.[26] It would be interesting to check whether the present approach can contribute to a deeper understanding of topology of this PES or it can predict possible PES modifications for appropriate diatomic molecules adsorbed on (111) faces of transition metals.

IV. CONCLUSIONS

By using topological notions (Betti numbers and Euler-Poincaré characteristic), the Morse theory puts limits on the number of critical points (extrema and saddle points) of functions on compact manifolds. In the present paper, the theory is applied to adsorption or diffusion of atoms and molecules on periodic crystalline surfaces. This application has an extremely simple character and can be employed to check the completeness and consistency of a proposed potential-energy surface of an adsorbate. The theory is yet more predictive when the substrate surface possesses high symmetry and/or some additional information such as the geometry of the stable adsorption site is available as we illustrate on examples from surface science. We show that for symmetric adsorbates and highly symmetric bcc and fcc(001) surfaces as well as fcc(111) or hcp(0001) ones, the set of critical points can be reduced to the highly symmetric sites on the surface when the saddle points coincide with the bridge sites. When in the latter sites the potential reaches an extremum, new sites must appear to host the saddle points. Other applications of the Morse theory in the solid-state physics are also shortly mentioned.

*Corresponding author. stepan.pick@jh-inst.cas.cz

[1] P. Hu, D. A. King, S. Crampin, M.-H. Lee, and M. C. Payne, J. Chem. Phys. **107**, 8103 (1997).

[2] A. Eichler and J. Hafner, Phys. Rev. B **57**, 10110 (1998), and references therein.

[3] E. D. German, M. Scheintuch, and A. M. Kuznetsov, J. Phys. Chem. C **112**, 15510 (2008).

[4] S. J. Jenkins and S. J. Pratt, Surf. Sci. Rep. **62**, 373 (2007).

[5] J. Milnor, *Morse Theory* (Princeton University Press, Princeton, NJ, 1961).

[6] V. A. Dubrovin, S. P. Novikov, and A. T. Fomenko, *Modern Geometry: Methods and Applications* (Springer, Berlin, 1990), Vol. 3, translated from Russian.

[7] http://en.wikipedia.org/wiki/Morse_theory (Wikipedia also offers information on other mathematical topics touched upon in the present paper).

[8] M. R. Peterson, I. G. Csizmadia, and R. W. Sharpe, J. Mol. Struct.: THEOCHEM **94**, 127 (1983).

[9] D. Liotard and M. Rérat, Theor. Chim. Acta **86**, 297 (1993); M. Rérat, D. Liotard, and J. M. Robine, *ibid.* **88**, 285 (1994), and references therein.

[10] T. Poston and I. Stewart, *Catastrophe Theory and Its Applications* (Pitman, London, 1978).

[11] D. Heidrich, W. Kliesch, and W. Quapp, *Properties of Chemically Interesting Potential Energy Surfaces* (Springer, Berlin, 1991).

[12] S. Sternberg, *Lectures on Differential Geometry* (Prentice Hall, Englewood Cliffs, NJ, 1964).

[13] Yu. A. Shashkin, *Euler Characteristic* (Mir, Moscow, 1984).

[14] S. Lefshetz, *Algebraic Topology* (American Mathematical Society, New York, 1942).

[15] M. Gajdoš, A. Eichler, and J. Hafner, J. Phys.: Condens. Matter **16**, 1141 (2004), and references therein.

[16] M. A. van Hove and S. Y. Tong, Phys. Rev. Lett. **35**, 1092 (1975).

[17] M. A. van Hove, S.-W. Wang, D. F. Ogletree, and G. A. Somorjai, Adv. Quantum Chem. **20**, 1 (1989).

[18] S. E. Mason, I. Grinberg, and A. M. Rappe, Phys. Rev. B **69**, 161401(R) (2004), and references therein.

[19] F. Abild-Pedersen and M. P. Andersson, Surf. Sci. **601**, 1747 (2007), and references therein.

[20] D. L. S. Nieskens, D. Curulla-Ferré, and J. W. Niemantsverdriet, ChemPhysChem **7**, 1075 (2006).

[21] A. M. Bradshaw and F. M. Hoffmann, Surf. Sci. **72**, 513 (1978).

[22] R. J. Behm, K. Christmann, G. Ertl, and M. A. van Hove, J. Chem. Phys. **73**, 2984 (1980).

[23] Q. Ge, P. Hu, D. A. King, M. H. Lee, J. A. White, and M. C. Payne, J. Chem. Phys. **106**, 1210 (1997).

[24] N. A. Deskins, J. Lauterbach, and K. T. Thomson, J. Chem. Phys. **122**, 184709 (2005).

[25] M. C. S. Escaño, T. Q. Nguyen, H. Nakanishi, and H. Kasai, Surf. Sci. **602**, 3415 (2008).

[26] A. Eichler, F. Mittendorfer, and J. Hafner, Phys. Rev. B **62**, 4744 (2000).