

Walter Langel

Walter Langel: Theoretical surface sciences: a microscopic perspective. Axel Groß, Advanced Texts in Physics, Springer Verlag, 2003, X, 275 pp. 105 illus., hardcover, ISBN: 3-540-43903-X, EUR 53,45

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For a long time the surface sciences and, especially, catalysis were considered to be closer to alchemy than to real science. During recent decades impressive experimental effort has led to a complete change in the situation. A variety of dedicated techniques, many based on electron scattering, has been introduced to the surface sciences. These yield detailed information about surface and adsorbate structure and spectroscopy on an atomic scale. A further breakthrough was the development of STM and AFM. Theoretical surface sciences mainly consist in the application of general concepts of chemistry and solid-state physics to the interpretation of typical surface spectroscopy experiments. Groß devotes his book to the analysis of surface structure and chemistry in terms of the electronic structure of substrate and adsorbate.

The first three chapters are an instructive and helpful introduction to current simulation techniques. Hartree–Fock and density-functional theory (DFT), including pseudo potentials and augmented plane waves and the semi-empirical tight-binding method, are explained with some focus on the periodicity of crystalline surfaces. The standard treatment of DFT is enhanced by a chapter on time-dependent DFT, which is the basis for treating electronically excited systems. Very important for the implementation of electronic-structure methods are pseudo potentials and the muffin tin wave functions, which are split in spheres around the nuclei and translationally invariant parts between them. Classical molecular dynamics simulation is treated in some detail later in the book, and force fields are presented implicitly as “parametrization of ab initio potentials”.

No appropriate reference is made, however, to first principles molecular dynamics, especially to the Car–Parrinello method. It has been applied to a variety of surface systems (not only of biological interest, as

wrongly stated in the book), and has very important advantages with regard to both classical molecular dynamics and static electronic structure calculations.

The electronic structure of a surface can be described in terms of electron densities, dispersion curves and local densities of states. This is laid out in Chaps. 4.1–4.3 and 4.5. for metals and semiconductors. Typically, a small number of localized states of the adsorbate interact with a nearly continuous distribution of electronic states in the substrate surface. Several models start from this assumption, including the Newns–Anderson model for chemisorption (Chap. 5.3), the bonding of H₂ to d-electrons in metals (Chap. 5.6) and the electron-friction model for scattering and sticking of molecules at the surface (Chap. 8.3).

Even AFM, which is usually regarded as purely mechanical scanning or even scratching of the surface, is sensitive to local electron densities of states. This is demonstrated for graphite where, by means of the Tersoff–Hamann model, information beyond the atomic structure was deduced from AFM scans. Further quantities, accessible by means of calculations on the electronic ground state are, e.g., work functions and surface energies for more or less relaxed structures. It would have been interesting at this point to find some reference to electron spectroscopy and diffraction methods such as UPS, XPS, LEED, or RHEED. These experimental techniques are of fundamental importance to the surface sciences, because of the small penetration depth of electrons, but the relevant theory is still not very intensively applied.

Chapter 8 discusses the fairly new field of calculations on electronically excited molecules starting with time-dependent density-functional theory (TDDFT). A major complication is that the electronic states in a molecule shift as a function of its distance from the surface, as is nicely demonstrated in Fig. 8.1. Probably the most relevant surface process in electronic excitation is photo-desorption, which is explained for NO on NiO. Here, even photoelectron spectra and state-specific velocity distributions can be obtained.

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Throughout the book mainly metal surfaces such as Pd, Pt, and Cu are considered, with some excursions to semiconductors such as Si. The intense work on ceramics and other oxide surfaces is poorly covered. Most examples feature H₂ and CO and some single atoms as adsorbates, which are the typical guinea-pigs of experimental surface sciences. It is mentioned only briefly in Chap. 9 that a wide range of much more interesting systems than just H₂ on Pd is handled by state-of-the-art calculations. The title of this chapter, “Perspectives”, is misleading, because calculations on H₂O, on solid liquid interfaces, on metal clusters and other catalysts, and on biomolecules on surfaces are nowadays standard for methods such as Car–Parrinello or periodic Hartree–Fock. Unfortunately, the book tends to give the impression to the reader that the theory is much further away from realistic applications than it really is.

All examples refer to crystalline substrates, because dedicated theories for the surfaces of amorphous materials do not seem to be available. The atomistic structure of the ordered surface is determined by the cleavage plane, which for each substrate crystal has only a few typical orientations. The freshly cleaved plane is often subjected to significant relaxation, which reduces the energy. DFT calculations can reproduce this phenomenon, which is discussed for a few examples such as silicon or Al₂O₃.

Another typical surface effect is the additional phonon density of states, usually described by the largely broadened “spaghetti” dispersion curves as shown in Fig 4.22 for a special silicon surface. Surface phonons were discussed in detail some years ago in a book by Kress and deWette, and are presented only very briefly here. The treatment in Chap. 4.6 refers implicitly to normal coordinate analysis and molecular dynamics simulation, which are the two standard methods for phonon calculations. In addition to cleaving, well-defined crystal surfaces can be generated by vapour deposition. The steps related to this process are discussed in much detail in Chap. 7.5 on an atomistic scale. This is a typical application of kinetic Monte–Carlo simulations, which are introduced at this opportunity.

An essential part of the book deals with the modelling of adsorption processes and surface reactions. Physical interactions between the substrate and the adsorbent are usually described by a potential, which has a simple form on a rigid and strictly periodic surface. In the book it is shown on several occasions how interaction potentials can be derived from the electronic structure of the system. The best known, but theoretically rather intricate, example is the van-der-Waals potential (Chap. 5.2).

A free particle impinging on such a surface is either scattered elastically or inelastically or sticks to it. The important quantity to be determined from this approach is the sticking coefficient (Chaps. 6.3–6.5), which can also be measured by use of molecular beams. An easier and more standard experiment for studying adsorption processes is temperature-programmed desorption (TPD).

The relationship of these spectra to the thermodynamics of the adsorption process is discussed in Chap. 7.4.

The potential model fails for chemisorption processes, for which the electronic structures of the system before and after adsorption have to be calculated explicitly. Examples are given in Chaps. 5.4, 5.5 and 5.7–5.9. Moreover, modern multi-particle methods recalculate the energy of the systems “on the fly” for each configuration attained, rather than working on predefined potential surfaces, whose importance does not seem to me as central as is claimed in Chap. 5.1.

The most challenging part of surface sciences is the description of reactivity, e.g. of catalysts. Chap. 7.1 gives an introduction to transition-state theory which is the most successful approach to rate constants. Its application enables calculation of partition functions and thus affords knowledge of electronic and vibrational states. The determination of the transition state itself is the most demanding part of the theory. It is only vaguely explained by reference to the nudged elastic band method, but the common approach, the search for a local energy maximum with one imaginary frequency, is not mentioned.

In contrast to transition-state theory molecular reaction dynamics affords multidimensional potential surfaces, along which trajectories are calculated. This approach is limited to small systems for which the complicated potentials can be evaluated. It is implicitly introduced in Chap. 6.6, where the most important types of surface reaction, dissociative adsorption and associative desorption, are discussed for H₂ on metals. Finally quantum dynamics using the full time-dependent Schrödinger equation are presented in Chap. 6.2 as the most general approach for reactive and non-reactive processes. No examples are given; only very few might yet be available.

These three kinetic concepts strictly refer to elementary reactions, whereas catalytic processes tend to be composed of a large number of competing or consecutive steps. Chap. 7.6 gives examples of this. Part of surface kinetics can be determined by two-dimensional diffusion processes (Chaps. 7.2, 7.3).

The text refers to an enormous wealth of different theories and approaches, and the theoretical concepts are very relevant for all surface scientists. The book in its present form is, however, simply too short for a conclusive and self-contained presentation of this ambitious field. From my understanding of the subject the contents deserve extension to at least twice the present volume.

It contains a number of specialised approaches to surface-relevant problems which are introduced with very different levels of explicitness. Very often only keywords are mentioned, and the discussion is based on special concepts which have not been properly introduced. Short paragraphs contain discussions which should include at least a drawing or a few formulae to enable basic understanding. The jellium model, for example, which plays a central role for electrons in

metals throughout this book, is introduced in exactly three sentences (p. 26): “Let us assume that the electrostatic potential of the electrons is compensated by a positive charge background. This is called the “jellium model”. Then the external potential and the Hartree potential exactly cancel: $v_{\text{ext}}(r) + v_{\text{H}}(r)$.” This is the type of explanation which is perfectly clear to the reader who is already familiar with the subject. In addition to that, the book, at least starting from Chap. 4, is not organized

in a way that the fundamental concepts and the relationship of the theory to key experiments are very easily deducible.

I think that the book in its present form, despite the very good exercises, can hardly serve as a textbook for any, even advanced, undergraduate courses. It is still highly recommended to surface scientists to have a look through and get an idea of the theoretical concepts available.