An Introduction to the Theory of Metal Surfaces

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1. Introduction

The purpose of this chapter is to provide a basic introduction, aiming at sharing what is known and, in some cases, what is not known about the physical properties and electronic structures of the important and interesting world of metal surfaces. By its very nature as an introductory text much of what we say will have been said before, though we will present it with our own personal and, hopefully, up-to-date perspective.

On the basis that one must understand clean surfaces before one can understand how they interact with their environment this chapter is limited entirely to clean metal surfaces. In addition, for reasons of space or because it is covered elsewhere in this volume there will be many interesting aspects of metal surfaces that will not be covered. Specifically, the metal surfaces we discuss will be flat and defect free; vibrations or any other dynamic properties will not be considered; more often than not the electrons we discuss will be sitting happily in their ground state. Magnetic and relativistic effects will largely be ignored and our periodic table will exclude elements with unfilled shells of f electrons. Setting this list of exclusions aside, there remains much to be said about the physical properties and electronic structures of metal surfaces. This will begin with a brief introduction to the most widely used electronic structure technique for interrogating the properties of metals and metal surfaces, namely density-functional theory. We then discuss cohesion in bulk metals, which serves mainly as a means to introduce important concepts and models used for bonding in metals such as densities of states, jellium, and tight-binding. The main body of the chapter then involves a discussion of the atomic structures of metal surfaces, their energies, and their electronic structures in turn. We close with some general conclusions and perspectives for future work.

2. A Beginner's Guide to Density-Functional Theory

2.1 Theoretical Framework

Density-functional theory (DFT) is the most popular and robust theoretical approach currently available for solving the electronic structures of solids and their surfaces. Although far from a panacea for all physical problems in this domain (or any other), no other theoretical approach has provided as much basic understanding of the electronic structures of surfaces, in general, and metal surfaces, in particular. DFT has proven capable of computing a host of properties of condensed matter and their surfaces to reasonable accuracy. What "reasonable" accuracy is and what properties can be determined will be discussed. But before this we briefly introduce the theoretical framework that lies behind DFT, and the approximations that must be made to make it work in practise. We limit this introduction to the very basics of DFT since this is, after all, a surface physics book and several excellent and detailed texts on the subject exist [1, 2]. The reader already schooled in the basics of DFT may jump to section 3.

The Hamiltonian within the Born-Oppenheimer approximation is

$$H = T^{e} + V^{nuc-nuc} + V^{e-nuc} + V^{e-e} \quad . \tag{1}$$

T^e is the kinetic energy of each of the N electrons given by,

$$-\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 \quad , \tag{2}$$

where ∇_i^2 is the Laplacian operator acting on each of the i electrons. $V^{nuc-nuc}$ describes the electrostatic interaction between the M ions (or nuclei) with fixed coordinates $\boldsymbol{R}_{J,\ldots N}$ and charges $Z_{J\ldots N}$

$$\frac{1}{2}\sum_{I \neq J}^{M,M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad . \tag{3}$$

V^{e-nuc} is the electron-ion interaction energy,

$$-\sum_{i,I}^{N,M} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_J|} \quad , \tag{4}$$

with electrons at positions r_i, and V^{e-e} is the electron-electron interaction energy given by,

$$\frac{1}{2}\sum_{i \neq j}^{N,N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad . \tag{5}$$

For simplicity and brevity in this section we use atomic units so that

$$e^2 = \hbar = m = 1 \quad , \tag{6}$$

where e is the electron charge, $\hbar$ is Planck's constant, and m is the electron mass.

The Hamiltonian can be written in one simple line as done above and slotted neatly into the Schrödinger equation,

$$H\Psi = (T^{e} + V^{nuc-nuc} + V^{e-nuc} + V^{e-e})\Psi = E\Psi \quad , \tag{7}$$

to deliver us the total energy of the system. The total energy of a given system at its ground-state, designated as E_0, is a highly sought after quantity. Many, if not most, physical properties of solids (or materials, in general) can be related to total energies or to differences in total energies.

However, solving the many-body Schrödinger equation is much easier said than done, and it is impossible to solve exactly for anything but the simplest model systems with 1, 2, or perhaps 3 electrons, or an infinite "jellium" system. Since solids contain lots ($\gg 10^{23}$) of electrons and the potential due to the nuclei is far from the constant of jelium we have a challenge. The root of the problem is well known. It is the quantity V^{e-e}, the electron-electron interaction, which contains all the many-body physics of the electronic structure problem. It depends on (at least) $3N$ spatial coordinates which are all coupled by the operator V^{e-e}.

There are many strategies for obtaining accurate approximate solutions to the many-body Schrödinger equation such as Green-function self-energy theory, quantum Monte Carlo, configuration interaction (CI), coupled cluster, and effective single-particle theories such as Hartree-Fock and DFT. The defining characteristic of DFT is that it aims to determine the ground state electron density distribution, n_0, of a system instead of the many-body wavefunction itself. Since real space is only 3 dimensional, regardless of the number of electrons in the system, the required minimization is with regard to only 3 variables and not $3N$ variables [3]. In principle DFT is thus most useful for many electron systems. Indeed density-functional simulations of systems with hundreds of electrons are now common and calculations with thousands of electrons are not unheard of.

Approaches for tackling the many body problem based on the density have been around since the 1920s [4, 5]. The birth of modern DFT for the electronic structure problem, however, came with the realization and associated proof by Hohenberg and Kohn in 1964 [6] that the ground state electronic wavefunction, Ψ_0, is a unique functional of the ground state electron density, n_0, i.e.,

$$\Psi_0 = \Psi_0[n_0] \quad . \tag{8}$$

We don't reproduce the proof of this theorem here since the original paper is of unimprovable brevity and clarity. However, we do point the interested reader in the direction of ref. [7] for a subsequent more general formulation.

From the Hohenberg-Kohn theorem it follows that all ground state observables are also functionals of the ground state density. In particular the ground state electronic energy, E_0^e, for a given configuration of the ions, is a functional, with a one to one correspondence, of n_0

$$E_0^e = E^e[n_0] = \min_{n(r)} \langle \Psi[n] | T^e + V^{e-nuc} + V^{e-e} | \Psi[n] \rangle \quad , \tag{9}$$

where the electron-nuclei interaction, which in this context is usually referred to as the "external potential", can be written explicitly in terms of the density as

$$V^{e-nuc}[n] = \int V(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \quad . \tag{10}$$

A variational principle, sometimes called the second Hohenberg-Kohn theorem, tells us that a successful minimization of the energy functional will yield the ground state density and the ground state total energy [8].

A critical problem with eqn. (9), however, is the evaluation of the kinetic energy functional. Although in principle T^e is a function of the density a direct evaluation is not feasible, at least not without introducing significant errors. A practical method for obtaining $E^e[n]$ and thus minimizing the functional came from Kohn and Sham with the application of the Lagrangian method of undetermined multipliers [9]. Hereby, one uses the fact that the functional in eqn. (9) can be written as a fictitious density functional of a *non-interacting* reference system

$$E^e[n] = T_s^e[n] + \int V(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\mathrm{Hartree}}[n] + E^{\mathrm{xc}}[n] \tag{11}$$

where $T_s^e[n]$ is the kinetic energy functional of non-interacting electrons of density distribution n. $E^{Hartree}$ is the Hartree energy describing the (classical) electron-electron Coulomb repulsion given by

$$E^{\mathrm{Hartree}}[n] = \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}' \quad . \tag{12}$$

And the final term, E^{xc}, is the exchange and correlation energy of DFT, into which all the complicated quantum-mechanical many-body effects are placed. The next step in this electronic structure problem in to define an effective potential,

$$\begin{aligned} V^{\mathrm{eff}}(\mathbf{r}) &= \frac{\delta\left\{\int V(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\mathrm{Hartree}}[n] + E^{\mathrm{xc}}[n]\right\}}{\delta n(\mathbf{r})} \\ &= V(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' + \frac{\delta E^{\mathrm{xc}}[n]}{\delta n(\mathbf{r})} \quad . \end{aligned} \tag{13}$$

from which one obtains the single-particle Schrödinger equation:

$$\left\{-\frac{1}{2}\nabla^2 + V^{\mathrm{eff}}(\mathbf{r})\right\}\varphi_{o_i}(\mathbf{r}) = \epsilon_{o_i}\varphi_{o_i}(\mathbf{r}) \quad , \tag{14}$$

which yields the orbitals that reproduce the density of the original many-body system

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_{o_i}(\mathbf{r})|^2 \quad . \tag{15}$$

This is an *effective* single-particle equation, because V^{eff} depends on the solutions that we are seeking. The Hartree and exchange-correlation potentials depend on $n[\mathbf{r}]$, which depends on the orbitals φ, which in turn depend on V^{eff}. Thus the problem of solving the Kohn-Sham equations (eqns. (13)-(15)) has to be done in a self-consistent (iterative) way. Usually one starts with an initial guess for $n(\mathbf{r})$, then calculates the corresponding V^{eff} and solves the Kohn-Sham equations for the φ. From these one calculates a new density and starts again. This procedure is then repeated until convergence is reached.

2.2 Approximations for Exchange and Correlation

So far, within the Born-Oppenheimer approximation, the theory is exact. However, we do not know the precise form of $E^{\mathrm{xc}}[n]$ and $V^{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E^{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}$ into which we have placed all the complicated many-body physics. As the name suggests $E^{\mathrm{xc}}[n]$ arises from a combination of two quantum mechanical effects: electron exchange and correlation. Briefly, electron exchange arises because a many-body wave function must by antisymmetric under exchange of any two electrons since electrons are fermions. This antisymmetry of the wave function, which is simply a general expression of the Pauli exclusion principle, reduces the Coulomb energy of the electronic system by increasing the spatial separation between electrons of like spin [10]. Likewise electron correlation further reduces the Coulomb energy between electrons of unlike spin because the motion of each individual electron is correlated with the motion of all others, helping also to keep electrons of unlike spin spatially separated. The sum of these two quantum mechanical effects as embodied in E^{xc} is incredibly difficult to describe. Indeed it is unclear if this functional can be given in a simple closed form at all. And so to get something useful out of DFT in practice one needs to approximate E^{xc}. There is no shortage of ways to do this, and as usual with a large number of anything, the anything gets categorized. Exchange and correlation functionals are no exception, being most often grouped in evolutionary terms (generations) or in biblical terms (the rungs of Jacob's ladder) [11]. Let's now look at some of the most popular types of exchange-correlation functional currently in use:

(a) *The local-density approximation (LDA)*: This is the simplest approximation, and can be written as

$$E^{\mathrm{xc-LDA}}[n] = \int n\epsilon^{\mathrm{xc-unif}}\left(n(\mathbf{r})\right)\, d^3\mathbf{r} \quad , \tag{16}$$

where $\epsilon^{\mathrm{xc-unif}}$ is the exchange-correlation energy per particle of the homogeneous electron gas of density n, i.e., the exchange-correlation energy density is taken to be that of a uniform electron gas of the same density. The exchange energy is known exactly and the correlation energy is obtained by fitting to the many-body studies of Gell-Man and Brueckner and Ceperly and Alder [12, 13]. Modern LDA functionals tend to be exceedingly similar, differing only in how their correlation contributions have been fitted to the many-body free electron gas data. The Perdew-Zunger (PZ) [14], Perdew-Wang (PW) [15] and Vosko-Wilk-Nusair (VWN) [16] functionals are all common LDA functionals [17].

Strictly, the LDA is valid only for slowly varying densities. Experience with calculations of atoms, molecules, and solids shows that eq. (16) can in general also be applied to these systems. Indeed LDA works surprisingly well and much current understanding of metal surfaces comes from LDA simulations. A partial rationalization of the success of LDA is provided by the observation that it satisfies a number of so-called sum rules [18–21].

(b) *The generalised gradient approximation (GGA)*: These are the second generation functionals (sitting on the second rung of Jacob's ladder) in which the gradient of the density, $\nabla n(\mathbf{r})$, at each coordinate is taken into account as well as the density itself:

$$E^{\mathrm{xc-GGA}}[n] = \int n\epsilon^{\mathrm{xc-unif}}\left(n(\mathbf{r})\right) \nabla n(\mathbf{r})\, d^3\mathbf{r} \quad . \tag{17}$$

Thus GGAs are "semi-local" functionals, comprising corrections to the LDA while (again) ensuring consistency with known sum rules. For many properties, for example geometries and ground state energies of molecules, GGAs can yield better results than the LDAs. Although, as we will see, for the properties of metals and their surfaces, GGA results are not necessarily superior to LDA results. The most widely used GGAs in surface physics are the PW91 [15] functional, and its close relative PBE [22]. PBE actually has several off-spring [23]; revPBE [24], RPBE [25], and PBE-WC [26]. RPBE is the most popular of the off-spring, although the latest addition to the PBE family, PBE-WC, offers promise for the simulation of solids and their surfaces.

(c) *The meta-GGAs*: These are the third generation functionals (third rung of Jacob's ladder) and use the second derivative of the density, $\nabla^2 n(\mathbf{r})$, and/or kinetic energy densities, $\tau_\sigma(n) = 1/2\Sigma_i|\nabla\varphi_i(n)|^2$, as additional degrees of freedom. In gas phase studies of molecular properties meta-GGAs such as the TPSS [27] functional have been shown to offer improved performance over LDAs and GGAs. However, aside from some benchmark studies of bulk materials and jellium surfaces, these functionals have not yet been exploited to any great extent in the solid state.

(d) *The hybrid functionals*: These fourth generation functionals add "exact exchange" calculated from Hartree-Fock (HF) theory to some conventional treatment of DFT exchange and correlation [28]. The most widely used, particularly in the quantum chemistry community, is the B3LYP [29] functional which employs three parameters, a_{1-3} (determined through fitting to experiment [11]) to control the mixing of the HF exchange and density functional exchange and correlation. It takes the following form:

$$E^{xc} = E^{xc-LDA} + a_1(E^{x-HF} - E^{x-LDA}) + a_2\Delta E^{x-GGA} + a_3\Delta E^{c-GGA} \quad . \tag{18}$$

Reformulating this to eliminate two parameters leads to an equation of the form

$$E^{xc} = E^{xc-GGA} + a(E^{x-HF} - E^{x-GGA}) \quad , \tag{19}$$

and setting $a = 1/4$ (based on the grounds of perturbation theory [30]) leads to a class of functionals with only as many parameters as their underlying GGAs. If PBE is the GGA used in eqn. (19) we arrive at the hybrid PBE0 functional [31]. Such functionals have been shown to offer noticeably improved performance over LDA and GGA functionals for the calculation of gas phase properties of molecules and band gaps in solids. However, applications of hybrid functionals to metals and metal surfaces are, as we will see, limited in number to only a few.

2.3 Other Approximations and Practicalities of Condensed Phase DFT calculations

Before we can take our electronic structure theory with our chosen exchange-correlation functional off to compute a metal or a metal surface there are several other issues to deal with and approximations to make. Good reviews exist on what it takes to perform a reliable condensed matter DFT simulation (see for example, refs. [32–34]), so we don't go into the details here, instead merely point out some of the relevant issues necessary to appreciate the discussion that comes later.

(a) *Periodicity and simulation cells:* A finite chunk of crystal contains many atoms; 10^{23} is not a large number when discussing the number of atoms in a crystal. Fortunately, crystalline solids have, by definition, periodicity. This periodicity introduces important elements of simplicity. Notably Bloch's theorem can be applied, allowing the electronic structure problem for infinite solids to be tackled in periodic 3D simulation cells, primitive or otherwise. Surfaces, although only periodic in two dimensions, can nonetheless be computed within periodic 3D simulation cells by introducing a vacuum region into the unit cell. In particular the introduction of a vacuum region along just one dimension, for example along the z axis in Fig. 1, partitions the unit cell into regions of solid (slab) and vacuum. The periodic boundary conditions ensure that the slab is infinite in the x and y directions, and also along the z direction the slab and vacuum stack extends infinitely. It

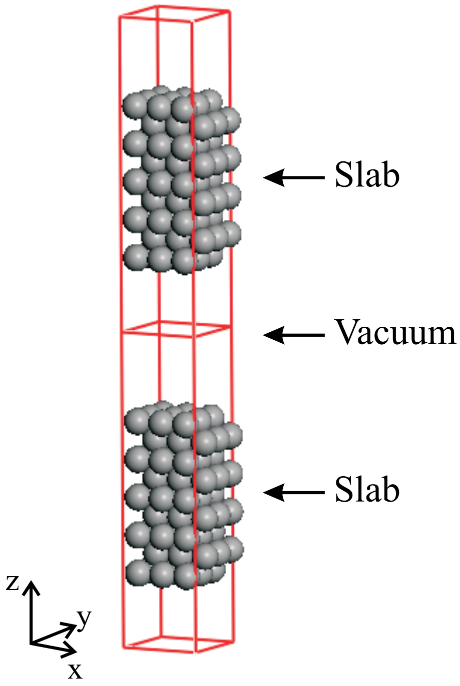


FIG. 1: Illustration of the supercell approach to model surfaces: the surface is represented by a periodic stack of slabs separated by vacuum.

is common to use this periodic slab model in simulations of metallic surfaces and results from such slab model simulations will be discussed frequently throughout this chapter [35].

(b) *Basis sets and electron-ion interactions:* The primary computational task in a DFT calculation is the solution of the Kohn-Sham equations for a given atomic structure and chemical composition. Invariably for a condensed phase system this requires the use of a set of basis functions with which to expand the Kohn-Sham orbitals φ. This choice of basis set is of critical importance to the accuracy of an electronic structure calculation; so much so that first-principles methods are often named according to the basis functions they employ.

Basis sets are constructed from either atom-centered functions or from non-atom-centered functions or a combination of both. For condensed phase simulations non-atom-centered basis sets such as plane waves are currently the most popular scheme. Often the choice of basis set goes hand in hand with the choice of electron-ion interaction and indeed if one chooses to use purely a plane-wave basis set one must replace the full and deep electron-ion potential with some approximate potential that can be described with a tractable number of plane waves. Hiding the core electrons in, for example, a pseudopotential (PP) or something similar like a projector augmented wave (PAW) potential are two possibilities [34, 36, 37]. And, indeed, the plane-wave plus PP or PAW recipe is currently the most popular one for electronic structure simulations of metals and their surfaces [34, 38]. Alternatively, one may choose to use a mixed basis set in which the computational cell is partitioned in to distinct regions, each of which is described with different basis sets. One particular scheme we mention here is the full-potential linearized augmented plane-wave (FP-LAPW) method [39]. In this scheme plane waves

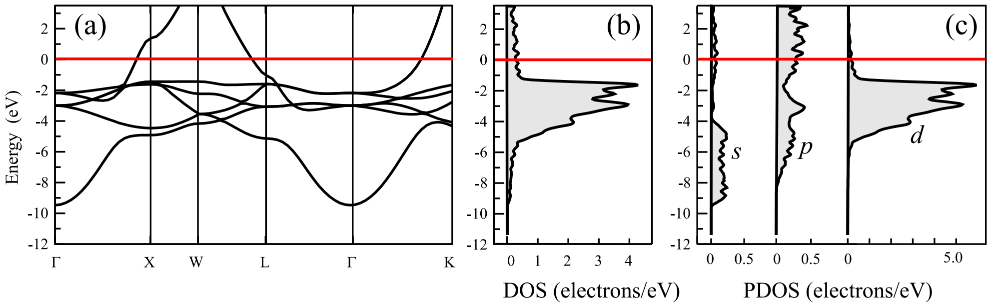


FIG. 2: Band structure (a), density of states (DOS) (b), and partial DOS (PDOS) (c) for bulk Cu as computed from a plane-wave pseudopotential DFT calculation within the LDA. In (c) the PDOS are projected onto Cu s, p, and d orbitals. The energy zero is the Fermi level (computed by the authors).

are used to describe a predefined interstitial region between the atoms in the solid and the regions close to the cores of the atoms, within predefined "muffin-tin" spheres, are described by radial functions and spherical harmonics. The FP-LAPW approach is more computationally expensive than the plane-wave plus PP or PAW approach, but has the advantage of being a truly all-electron approach. In many cases in solid state systems FP-LAPW calculations thus provide the benchmark "gold standard" theoretical data with which to compare other methods. Where possible in the following we will thus discuss results from FP-LAPW calculations.

3. Cohesion in Metals: Elementary Concepts and Ideas

Before tackling metal surfaces, let's first recall some basic features of bonding and cohesion in bulk metals. We first introduce simple models for bonding such as jellium and tight binding and then assess our theoretical tool of choice, DFT, at predicting some of the central cohesive properties of metals.

3.1 Metallic Bonding and Densities of States

The essential characteristic of metallic bonding is that the valence electrons are delocalized among a lattice of metal atoms. Delocalization is the consequence of heavy overlap between the individual valence wavefunctions resulting in the valence electrons being shared by all the atoms in the "community". In most abstract terms, metals can thus be perceived as atomic nuclei immersed in a featureless sea (or "glue") of electrons. This electron sea leads to bonding that is generally not directional, resulting in close-packed crystal structures being often favored, such as the fcc and hcp structures. Because of the strong overlap of the orbitals the resultant electronic wavefunctions or bands of a metal will thus exhibit a strong dispersion in reciprocal space, $\boldsymbol{k}$ space. As an example we show in Fig. 2(a) the band structure of bulk Cu.

A useful quantity for interpreting the characteristics of chemical bonding, that we will use throughout to examine metals, is the density of states. It is defined as

$$N(\epsilon) = \int n(\mathbf{r}, \epsilon) d\mathbf{r} = \sum_{i=1}^{\infty} \delta(\epsilon - \epsilon_i) \quad , \tag{20}$$

where the sum goes over all eigenstates (orbitals) with eigenvalues, ϵ_i of the Kohn-Sham Hamiltonian. Cutting through this DOS is the Fermi level (E_F): the energy below which the one-electron levels are occupied and above which they are not, in the ground-state of a metal. Again we illustrate these concepts with the the example of Cu, displayed in Fig. 2(b). For future reference, we note that for metals at 0 K the Fermi level is equivalent to the chemical potential of the electrons.

Another useful quantity, which is not readily accessible in any simple manner from experiment, is the state-resolved DOS, also called the projected DOS (PDOS):

$$N_\alpha(\epsilon) = \sum_{i=1}^{\infty} |\langle \phi_\alpha | \varphi_i \rangle|^2 \delta(\epsilon - \epsilon_i) \quad , \tag{21}$$

where ϕ_α is a properly chosen localized function whose overlap with the Kohn-Sham orbitals is determined. Often it proves useful to pick individual atomic orbitals or groups of atomic orbitals as localization functions upon which to project the electron density. For example, we have done this for Cu in Fig. 2(c) from where it can be seen that the Cu valence band is comprised of *s*, *p*, and *d* states.

3.2 Simple Metals and Jellium

It turns out that for the *s* and *p* block metals a simple model, namely the *jellium model* provides useful insight. In this model the discrete nature of the ionic lattice is replaced with a smeared out uniform positive background exactly equal to that of the valence electron gas. In jellium, each element is completely specified by just the electron density $n = N/V$, where N is the number of electrons in the crystal and V is its volume. Usually the electron density is given in terms of the so-called *Wigner-Seitz radius*, r_s, where $r_s = (3/4\pi n)^{1/3}$ which corresponds to the spherical volume in Bohr atomic units available to one valence electron. The r_s of real metals range from ~ 2 (high density) to ~ 6 (low density).

For the completely smeared out constant ion density of jellium the electron-ion, ion-ion, and Hartree energies cancel exactly ($E^{e-nuc} + E^{nuc-nuc} + E^{Hartree} = 0$) leaving,

$$E/N = T_s + E^{xc} \quad , \tag{22}$$

where, à la DFT, T_s is the kinetic energy of the non-interacting electron gas and E^{xc} is the exchange and correlation energy. It is easy to show that the kinetic energy of the free electron gas is, in atomic units, $T_s = \frac{2.21}{r_s^2}$ [40, 41]. The exchange energy per particle can also be computed exactly from HF theory and together with accurate parameterizations of the correlation energy, the binding energy of jellium (in atomic units) is

$$E/N = \underbrace{\frac{2.21}{r_s^2}}_{T_s} \underbrace{- \frac{0.916}{r_s} - 0.115 + 0.0313 \ln r_s}_{E^{xc}} \quad . \tag{23}$$

The kinetic energy contribution to eqn. (23) is, of course, positive and repulsive, whereas the contribution from electron exchange and correlation is attractive. The latter is the glue that hold metals together and arises from the formation of the so-called exchange-correlation hole. This is a region of charge depletion around each electron due to the fact that electrons of like spin keep apart because of the antisymmetry condition and the motion of electrons of unlike spin is correlated (section 2.2). The main consequence of this region of charge depletion around each electron for the present discussion is that each electron feels an attractive potential from the surrounding positive jellium background. Therefore the equilibrium bound state of minimum total energy results from a balance between the kinetic energy of the valence electrons, which tries to push the atoms apart, and the exchange-correlation energy, which tries to pull them together. The minimum in this binding energy curve for jellium occurs at an $r_s = 4.2$ with a binding energy of 2.2 eV/atom. This is quite close to the cohesive energy, E^{coh}, of real *sp* metals which fall at around 1-2 eV/atom [42] and quite good agreement considering the simplicity of the model. Indeed jellium can be modified [40, 43–45] to do better and to describe a range of properties (for example, phonon spectra, optical absorption, superconducting transition temperatures, and equations of states) by replacing our initial approximation of a uniform positive background with something less extreme, like, for example, a weak pseudopotential.

3.3 Transition Metals and Tight Binding

The transition metals belong to three series in the periodic table which correspond to the progressive filling of $3d$, $4d$, and $5d$ states. The presence of the d electrons changes the picture of bonding in these metals considerably from the simple metals and the jellium description of metallic bonding no longer suffices. Notably the cohesive energies rise to significantly more than the 1-2 eV/atom of the simple metals and follow a roughly parabolic variation across the transition metal series. For example, E^{coh} goes from 4.36 to 6.66 to 3.92 eV/atom from Y to Ru to Pd [46].

To understand this variation in E^{coh} it is useful to recognize that the electronic structure of the transition metals is comprised of two largely separate contributions: a broad free-electron-like *sp* band; and a considerably narrower d band. We saw this already with the PDOS plot of Cu (Fig. 2) and we illustrate it again schematically in the top part of Fig. 3(a). The d band is narrower than the *sp* band simply because the d valence orbitals and thus the overlap between them is significantly smaller than the s and p valence orbitals. For example, the peak maximum of the $3d$ radial distribution for the $3d$ transition metals is typically >2 times closer to the core than the peak maximum of the $4s$ radial distributions [47]. For such systems where there is small overlap between orbitals a tight-binding description in which the system is described by a simple linear combination of atom centered d orbitals can be used. The simplest version of this applied to the transition metals is the the so called *rectangular d band model* of Friedel, where the d PDOS is assumed to be rectangular and E^{coh} takes the following form

$$E^{\mathrm{coh}} \propto \frac{W}{20} N_d (N_d - 10) \quad , \tag{24}$$

where W is the width of the d band and N_d is the number of d electrons. As one can see from eqn. (24) this model leads to a parabolic shape for the cohesive energy over the transition metal series and suffices at catching the basic chemical behavior that as one

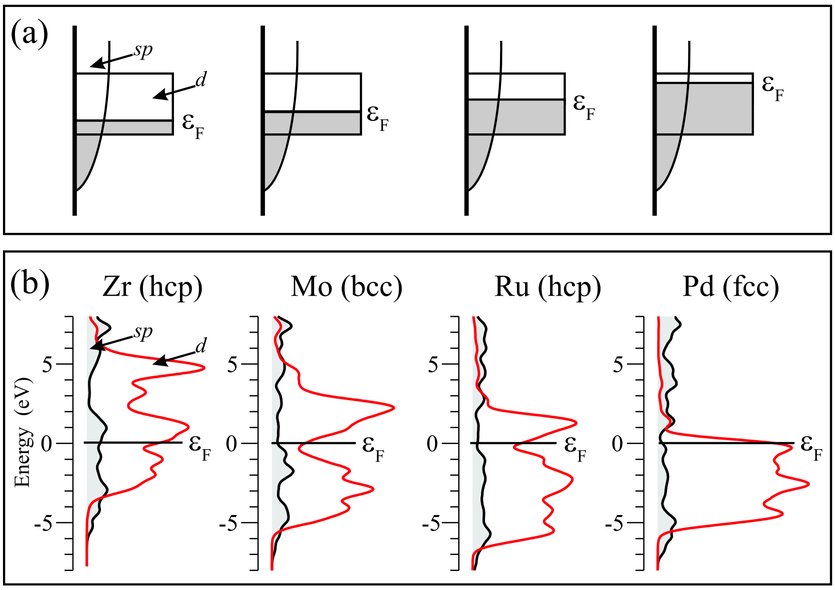


FIG. 3: (a) Schematic illustration of the relative filling of the *d* and *sp* densities of states as one moves from left to right across the transition metals. (b) Computed *d* and *sp* partial densities of states for several 4*d* transition metals, as obtained from a plane-wave pseudopotential DFT calculation within the LDA (computed by the authors).

moves from left to right across the transition series one gradually fills up the *d* band, which, of course, involves filling the bonding, non-bonding and then anti-bonding states until finally at the end of the transition metal series, the *d* band is completely filled. We illustrate this progression schematically Fig. 3(a). This crude model captures the qualitative cohesive trend over a large number of elements and with a suitable choice of the parameter W and the introduction of an (empirical) proportionality constant to account for repulsion between the ions in the solid, also the absolute cohesive energies come out quite well. For the interested reader a detailed discussion on this topic can be found in the book by Desjonquères and Spanjaard [48].

We will see when we move to surfaces that the rectangular *d* band model helps to explain trends in surface electronic structures also. However, it must be recognized that this is merely a highly simplified model of the electronic structures of transition metals. In reality the DOS results from an integration over the Brillouin zone and so points that occur often and where the bands are relatively flat will give rise to a high density of states. This implies that the detailed shape of the *d* DOS is more complex that the simple rectangular model assumes and reflects the lattice type of the crystal rather than the filling. This can be seen in Fig. 3(b) where PDOS from self-consistent DFT calculations are shown for four 4*d* metals (Zr, Mo, Ru, and Pd). The *d* PDOS of the fcc metal Pd is rather similar to the *d* PDOS of Cu (also fcc) (Fig. 2). The two hcp metals Zr and Ru exhibit similar *d* PDOS and the bcc metal metal Mo, exhibits a large dip in the center of the *d* PDOS characteristic of bcc metals [49]. Despite the added complexity, however, it can be seen from Fig. 3 that the trend embodied in the rectangular *d* band model with regard to *d* band filling holds, which is, of course, the reason for the qualitative success of the model.

3.4 DFT for the Cohesive Properties of Metals?

Simple models aside, if we choose to perform a self-consistent DFT calculation in which we explicitly treat the ionic lattice with, for example a pseudopotential or full potential treatment, what level of accuracy can we expect to achieve? As always the answer depends on the properties we are interested in and the exchange-correlation functional we use. DFT has been used to compute a whole host of properties of metals, such as phonon dispersion curves, electronic band structures, solid-solid and solid-liquid phase transitions, defect formation energies, magnetism, super-conducting transition temperatures, and so on. However, to enable a comparison between a wide range of exchange-correlation functionals, we restrict ourselves here to a discussion of only three key quantities, namely (i) E^{coh}; (ii) a_0, the equilibrium lattice constant; and (iii) B_0, the bulk modulus.

Table 1 lists a number of DFT and experimental values for a simple metal Al, two noble metals Pd and Ag, and a transition metal with an unfilled *d* shell Pd. One example from each of the first four generations of exchange-correlation functional is given so as to provide a flavor of the current state of DFT for the cohesive properties of metals. In addition to the LDA we show results from the PBE (GGA), TPSS (meta-GGA), and PBE0 (hybrid) functionals. Let's consider each functional in turn and see what general conclusions can be drawn:

(a) LDA predicts the smallest lattice constants, the largest bulk moduli, and the largest cohesive energies. Moreover, compared to experiment the LDA lattice constants are smaller (~ -2 %), the bulk moduli are larger ($\sim +10$ %), and the cohesive energies are larger ($\sim +20$ %) for these four materials. These quantities are naturally all related and reflect the now well-established fact that LDA generally over binds metals (and other solids and molecules).

(b) The PBE (GGA) functional results are generally closer to experiment than LDA. The average errors for these metals are $+1.3$ % for the lattice constants, and -5 % for both the bulk moduli and cohesive energies. Naturally this improvement leads to larger lattice constants, smaller bulk moduli, and smaller cohesive energies. For the late transition metals and the noble metals this actually results in an over-correction with GGA-PBE predicting too large lattice constants and too small cohesive energies.

(c) The TPSS (meta-GGA) functional is somewhat difficult to assess. For lattice constants it is significantly better than LDA and GGA with an error of only 0.5 %, getting all four metals within 0.04 Å. For the bulk moduli, however, it is not as accurate with an error of 11 %, and unfortunately, E^{coh} has not yet been computed for these metals (or any other metals) with this functional [53].

(d) The hybrid PBE0 functional does not appear to offer any clear improvement over the other functionals. At an error of 1 % for the lattice constants PBE0 performs worse than TPSS and is similar to PBE. Furthermore, errors for the bulk moduli and cohesive energies, both of 10 % are rather disappointing; offering worse performance than the regular GGA-PBE [54]. Since using functionals with exact exchange when treating solids (or more precisely periodic systems) generally leads to a considerable increase in computational effort (about a factor of 35 with a plane-wave basis set according to

TABLE 1: Bulk properties of Al, Cu, Pd, and Ag, as computed from DFT with the LDA, PBE, TPSS, and PBE0 exchange-correlation functionals. All data is taken from Refs. [50], [51], and [52]. Ref. [50] is an all-electron study with a Gaussian basis set. Data from ref. [51] has been obtained with the plane-wave plus PAW method and data from ref. [52] has been obtained with the FP-LAPW method.

		a_0(Å)			B_0 (Mbar)			E^{coh} (eV)		
		Ref. [50]	Ref. [51]	Ref. [52]	Ref. [50]	Ref. [51]	Ref. [52]	Ref. [50]	Ref. [51]	Ref. [52]
Al	LDA	4.01		3.98	0.82		0.84			4.07
	PBE	4.06	4.04	4.04	0.76	0.77	0.78		3.43	3.60
	TPSS	4.04			0.85					
	PBE0		4.01			0.86			3.39	
	expt.		4.03			0.79			3.39	
Cu	LDA	3.53		3.52	1.88		1.92			4.57
	PBE	3.64	3.64	3.63	1.50	1.36	1.42		3.48	3.51
	TPSS	3.59			1.71					
	PBE0		3.64			1.30			3.05	
	expt.		3.60			1.42			3.49	
Pd	LDA	3.85		3.85	2.35		2.22			5.04
	PBE	3.95	3.94	3.95	1.77	1.66	1.63		3.71	3.63
	TPSS	3.92			2.00					
	PBE0		3.92			1.72			2.88	
	expt.		3.88			1.95			3.89	
Ag	LDA	4.00			1.49					
	PBE	4.13	4.15		1.06	0.89			2.52	
	TPSS	4.08			1.27					
	PBE0		4.14			0.87			2.33	
	expt.		4.07			1.09			2.95	

one recent estimate [55]) it is difficult to justify their use if one is purely interested in determining properties such as the lattice constant, bulk modulus and cohesive energy of metals. In addition other hybrid functionals, such as B3LYP, can perform even worse [56], with, for example, the computed E^{coh} of Cu differing from experiment by $>$30 % [57].

In conclusion, of the functionals tested, no single one stands out as being significantly superior to the others for treating metals. All of them perform reasonably well in capturing the large variation in lattice constants and bulk moduli. Periodic trends in E^{coh} are also reproduced. As for the quantitative determination of E^{coh}, however, the situation is far from satisfactory with the choice of exchange-correlation functional crucial to the value obtained. Moreover, there is no convincing proof to tell us that, for example, GGA will always be superior to LDA. The identification of a functional, or, indeed any electronic structure method that is computationally efficient and consistently able to calculate E^{coh} for metals with an accuracy of, for example, less than 5 % error remains an important unresolved issue in materials science.

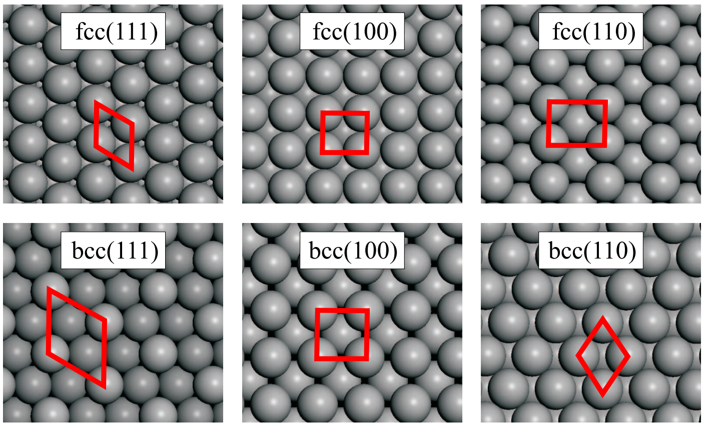


FIG. 4: Structures of some (unreconstructed) low Miller index surfaces of fcc and bcc metals. The surface unit cell is shown in each case. The density of surface atoms decreases from left to right for the fcc surfaces and from right to left for the bcc surfaces.

4. Basics of Metallic Surfaces

4.1 Surface Structure

Knowledge of the atomic arrangement in the surface region is a prerequisite to understanding the properties of surfaces, and so let's now briefly consider the structures of metallic surfaces. As we know metals come most often in fcc, hcp, or bcc structures. Of the many ways to cleave such crystals to produce a surface the most interesting to us here are those with low energy. These tend to be close-packed surfaces such as the (111), (100) or (110) surfaces of fcc and bcc metals, or the (001), (100), and (101) surfaces of the hcp metals. For orientation purposes we show the structures of the aforementioned fcc and bcc surfaces in Fig. 4.

Because the atoms at the surface of a crystal have less neighbors than they do in the bulk it is unlikely that they will remain at their precise "bulk truncated" positions. Rather, the atoms are likely to move in response to their new environment. Minor displacements in which the top few layers of metal atoms move inward or outward along the surface normal, but retain their periodicity parallel to the surface, are generally referred to as *surface relaxations*. More pronounced alterations of the atoms in the surface region involving lateral displacements which alter their translation symmetry parallel to the surface and/or changes in the surface layer atomic density are generally known as *surface reconstructions*. We illustrate the distinction between surface relaxations and surface reconstructions in Fig. 5 and now discuss some examples of each type of behavior.

4.1.1 Surface Relaxation

Many close-packed metal surfaces undergo a simple relaxation in which only the interlayer spacings of the top layer or so change. For such systems the well-known model of Finnis and Heine is applicable and used to rationalize how the surface atoms can be expected to relax [58]. This model predicts: (i) a small *contraction* for the first interlayer spacing;

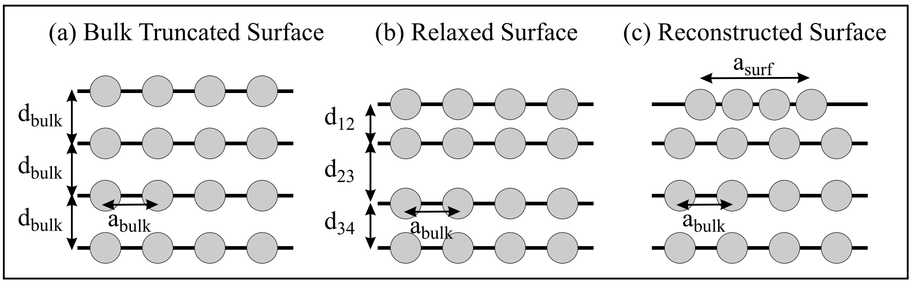


FIG. 5: Schematic side views of: (a) a bulk truncated surface; (b) a relaxed surface; and (c) a reconstructed surface.

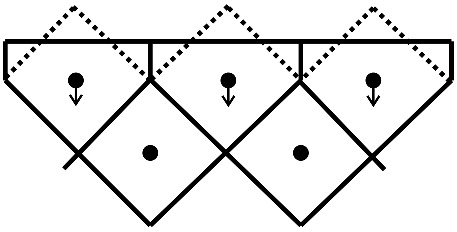


FIG. 6: Illustration of the Finnis-Heine model for interlayer relaxation at metal surfaces. See text for details (after ref. [58]).

and (ii) that the contraction is more pronounced for open surfaces than for close-packed ones. The original application was to the low Miller index surfaces of Al, for which contractions of 2, 5, and 16 % were predicted for the (111), (100), and (110) surfaces, respectively. Such contractions were not inconsistent with experimental observations at the time [59–61].

The physical basis of the model is the Smoluchowski smoothing of the electron charge density at the surface [62]. When a crystal is cut to form a surface, the electrons rearrange in order to reduce the charge-density corrugations and by this way their kinetic energy. This leads to a motion of the electrons left on top of the surface atoms downward to the crystal resulting in an electrostatic attraction of the top layer ions toward the rest of the crystal. This is illustrated schematically in Fig. 6. As electronic corrugations are rather flat for close-packed surfaces, small contractions are expected in that case. For more open surfaces larger contractions can be expected. Landman *et al.* [63] subsequently expanded the model to show that the redistribution of electronic density extends over several layers, giving rise to a tendency for a damped oscillatory nature to the relaxation. Indeed for Al(110) subsequent low-energy electron-diffraction (LEED) analysis confirmed the prediction of multilayer relaxation [64], thus representing an early success for the predictive nature of electronic structure theories in their application to the structure of surfaces.

The model as outlined above, however, is not as general as one might be lead to expect, and not as widely applicable as it is often said to be [65, 66]. In particular the closest packed hexagonal surfaces of the fcc and hcp metals often undergo an “anomalous” expansion of the first to second layer distance relative to the bulk interlayer spacing. This is clear from Table 2 where measured interlayer relaxations at a number of hexagonal

TABLE 2: Percentage interlayer relaxations, Δd_{ij}, for several (unreconstructed) close-packed hexagonal metal surfaces, as obtained from DFT (LDA and PBE) calculations and LEED analyses. All data is from ref. [52].

		Al(111)	Ti(0001)	Cu(111)	Pd(111)	Pt(111)
Δd_{12}	LDA	+1.35	-6.44	-1.58	-0.22	+0.88
	PBE	+1.35	-6.84	-1.19	-0.01	+1.14
	LEED	+2.2 ± 1.3	-2.1	-0.7 ± 0.5	+1.3 ± 1.3	+0.87
	LEED	+0.9 ± 0.5	-4.9	-0.3 ± 1.0	+2.4 ± 0.9	+1.20
	LEED	+1.7 ± 0.3				+1.0 ± 0.1
	LEED	+1.3 ± 0.8				+1.0
Δd_{23}	LDA	+0.54	+2.64	-0.73	-0.53	-0.22
	PBE	+0.54	+2.82	-0.65	-0.41	-0.29
	LEED	+0.5 ± 0.7	+1.4		-1.3 ± 1.3	
	LEED				+0.7 ± 0.9	
Δd_{34}	LDA	+1.04	+0.37	-0.43	-0.33	-0.17
	PBE	+1.06	-0.51	-0.24	-0.22	-0.21
	LEED		-1.1		+2.2 ± 1.3	
	LEED				+0.7 ± 1.8	

close-packed metal surfaces are listed. This table includes the results of DFT (LDA and PBE) calculations and LEED analyses for simple, noble, and transition metals aiming at providing a broad and representative overview of the behavior of close-packed metal surfaces. It can be seen from the table that LEED predicts an expansion of the first to second interlayer spacing of Al(111), Pd(111), and Pt(111). For two of these surfaces (Al and Pt) there is excellent agreement between theory and experiment suggesting that the expansion is a real effect. For Pd(111) and some other surfaces not listed in Table 2, such as Rh(111) and Ru(0001), experiment and theory disagree and the question of how exactly the topmost layer relaxes is still somewhat unclear [67–69].

4.1.2 Surface Reconstruction

For many surfaces the displacements of the atoms from their bulk truncated positions are more pronounced than a simple relaxation in which only the interlayer spacings change. These may involve lateral displacements of atoms within the surface layers and/or a change in the surface layer atomic density. In Fig. 7 we show three well-known examples of the common types of reconstructions observed for clean metal surfaces. Following Titmuss *et al.* [70] we discuss these examples as representative of three classes of reconstruction that may occur at metal surfaces:

(a) *Displacive reconstructions at constant layer density*: Some surfaces undergo displacive intralayer lateral relaxations within the surface layers, lowering the layer symmetry but not the density. Within this class of displacive reconstructions the c(2×2) reconstruction of W(100) is the most well characterized. As illustrated in Fig. 7(a) the top layer of W atoms reconstructs from the ideal square lattice to a “zigzag” atomic arrangement. This is achieved through a pair of symmetry breaking lateral displacements as indicated by the arrows in the top part of Fig. 7(a). LEED structural analysis gives a lateral displacement

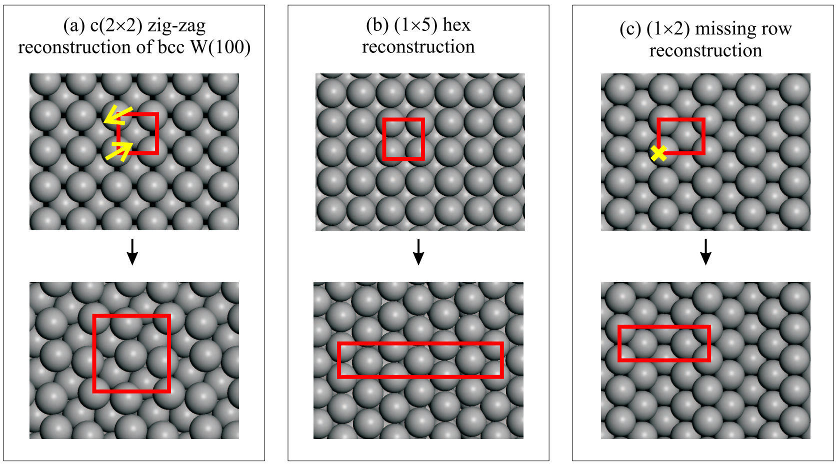


FIG. 7: Illustration of three bulk truncated surfaces and typical types of reconstruction that they undergo. (a) depicts the (1×1) to $c(2 \times 2)$ reconstruction of bcc W(100). The arrows indicate the direction in which the top layer W atoms move upon reconstruction. (b) displays an example of the "hex" reconstruction that the late $5d$ (fcc) transition metals undergo. The specific example is the (1×1) to (1×5) reconstruction of fcc Ir(100). (c) displays the (1×1) to (1×2) "missing row" reconstruction that occurs on the (110) surfaces of the late $5d$ (fcc) transition metals. The rows of atoms removed by the reconstruction are indicated by the × at the edge of the unit cell.

of the top layer W atoms of ~ 0.2 Å [71–74]. Although not apparent from Fig. 7(a) this reconstruction also involves displacements of the sub-surface W atoms as well as a contraction of the topmost interlayer spacing of 6 %. The results obtained from DFT LDA calculations are consistent with the experimentally determined structural model and point to a coupling between one of the surface states of W(100) and a particular surface phonon mode as the origin of the reconstruction [32, 75].

(b) *Changes in surface layer atomic density*: Large-scale surface reconstructions producing changes in the surface layer density have been identified on several metal surfaces. Notably the top layer of the (100) surfaces of Pt, Au, and Ir reconstruct from their ideal square arrangements into quasi-hexagonal configurations known as "hex" phases [76–83]. Because of the different symmetries of the reconstructed top layer and the substrate, generally commensurate hex phases have rather long periodicities; (5×1) and (20×5) surface unit cells have been observed. Indeed the (5×1) periodicity, which takes place on Ir(100), is the simplest of the hex reconstructions found and the one displayed in Fig. 7(b). Again this reconstruction involves displacements of subsurface atoms and a change in surface interlayer distances. Based on DFT calculations Fiorentini *et al.* [84] suggested that the driving mechanism for this class of reconstruction is the tensile excess stress present in the unreconstructed surfaces. This explanation, which finds its origin in a depletion of d charge from the surface layer, also explains why the $4d$ isoelectronic upper neighbors of Pt, Au, and Ir, i.e., Rh, Pd, and Ag, do not reconstruct.

Another surface reconstruction that fits happily into this class of reconstructions is the so-called herring bone reconstruction of Au(111) [85–89]. Here a uniaxial contraction along one of the $\langle\bar{1}10\rangle$ directions in the top layer leads to a layer with a higher density of atoms in it than the unreconstructed (111) surface and a surface unit cell of $(n \times \sqrt{3})$

($n = 22$).

(c) *Missing row reconstruction of fcc (110) surfaces*: A well-known class of reconstruction is the so-called missing row reconstruction of the fcc (110) surfaces [90–94]. The (110) surface is the most open of the widely studied low Miller index fcc surfaces. Consequently, it has the lowest surface layer atomic density and the highest surface energy, making it the most likely to reconstruct. In the case of Ir, Pt, and Au the clean (110) surface spontaneously reconstructs, giving rise to the the (1×2) missing row reconstruction. As the name suggests every second close-packed row along the (110) surface is removed (Fig. 7(c)), resulting in a surface comprised of ribbons of (111)-like microfacets. On closer inspection, LEED as well as DFT find that each of the missing row reconstructed surfaces show all three effects discussed above: a relaxation of the first to second interlayer distance; a change in the surface layer atomic density; and a displacive reconstruction of some of the surface layers parallel to the surface. For the interested reader ref. [95] and references therein provides a more detailed discussion of this particular type of reconstruction for the specific case of Pt(110).

To conclude, surfaces tend *not* to retain their bulk-truncated structures. Most surfaces undergo a multilayer relaxation driven by the movement of surface atoms into new locations. However, a variety of other displacements and reconstructions are possible and occur. Again the interested reader may wish to refer to Tables 2.3a and 2.3b of Somorjai's textbook on surface chemistry for a more complete overview of the many and varied structures clean metal surfaces can adopt [65].

4.2 Surface Energetics

4.2.1 Introduction and Experimental Considerations

The energy to make a surface at a given temperature and pressure is the *Gibbs surface free energy*, G^S. The Gibbs surface free energy thus determines the surface that will form under real world everyday conditions, and can be defined by the relation

$$G = NG^0 + AG^S \quad , \tag{25}$$

where G is the total free energy of the solid, N is the number of atoms in it and A is the surface area [65, 96]. Thus G^S is the excess free energy that the solid has over the value G^0, which is the value per atom in the infinite solid. Excess implies that G^S is a positive quantity, i.e., it costs free energy to make more surface. For *elemental* systems and in the absence of an applied electrical field this is always the case. For binary, ternary or more complex materials, in which the precise stoichiometry of bulk and surface phases becomes unclear, there have been suggestions that G^S need not be positive under all conditions [97, 98].

The Gibbs surface free energy will usually be different for different facets of a crystal. Such variations, often referred to as surface free energy anisotropies, are key to determining the equilibrium crystal shape (as well as many other properties) of materials because at equilibrium a crystal seeks to minimize its total surface free energy subject to the constraint of constant volume.

To see exactly how variations in G^S impact upon the equilibrium crystal shape of materials let's now examine a simple 2D model system. Consider the schematic (ccp-like) crystal shown in Fig. 8(a). One can imagine different planes along which to cleave this crystal to produce a surface. Some possible cuts are indicated in Fig. 8(a) and are labeled by the angle, Θ, that they make with the [01] plane. Clearly, in this model system, cuts along $\Theta = 0°$ and $\Theta = 90°$ will yield identical close-packed surfaces, cleavage along the plane $\Theta = 45°$ will also yield a close-packed surface but with a lower density of atoms in the top layer, and cleavage along the planes $\Theta = 22.5°$ and $\Theta = 67.5°$ will produce the most corrugated (stepped) surfaces. Generally the surface energy increases with the corrugation of the surface, something we will discuss in more detail below, and thus one can expect that surfaces cut along the planes $\Theta = 0°$ and $\Theta = 90°$ will have the smallest surface energy and surfaces cut along the planes $\Theta = 22.5°$ and $\Theta = 67.5°$ will have the largest surface energy with $\Theta = 45°$ coming somewhere in between. A so-called polar surface energy plot provides a particularly convenient and concise way in which to represent the dependence of G^S on Θ, $G^S(\Theta)$, and is a useful first step towards determining the equilibrium crystal shape. In Fig. 8(b), the first quadrant of one such plot for the model system shown in (a) is displayed. Such plots are constructed by drawing radial vectors from the origin with a magnitude proportional to G^S for each value of Θ. Thus for the simple model in Fig. 8(a) the magnitude of $\overrightarrow{G}^S(0)$ is relatively small, $\overrightarrow{G}^S(22.5)$ and $\overrightarrow{G}^S(67.5)$ are relatively large and $\overrightarrow{G}^S(45)$ is somewhere in between. From such a polar surface energy plot it is then straightforward to determine the equilibrium crystal shape by applying the Wulff theorem or by, in other words, performing a Wulff construction [99]. The aforementioned Wulff theorem is remarkable in two respects: its simplicity to apply and its difficulty to prove [100]. Here, we deal with the application, which tells us to construct planes (or lines in this 2D example) at the endpoints of and perpendicular to the radial G^S vectors (Fig. 8(c)). The resultant planes (lines) are known as Wulff planes (lines) and it is simply the inner envelope - the inner Wulff envelope - of all the planes (lines) connected normal to the vectors of the surface energy plot that yields the equilibrium crystal shape (Fig. 8(d)). The resultant 2D crystal shape obtained by performing a Wulff construction on all four quadrants of a polar surface energy plot for the model system in Fig. 8(a) is shown in Fig. 8(d).

Before moving away from Wulff constructions, we briefly make a few rather self-evident but nonetheless worthwhile comments upon it. First, the distance of each face from the center of the crystal is proportional to the surface energy of that face. The equilibrium crystal shape for a purely isotropic crystal is thus a sphere. Second, the Wulff theorem can be used in "reverse", i.e., given a crystal of a particular shape one can use the Wulff theorem to extract the relative surface energies of the different facets exposed. This is a powerful and commonly used technique for extracting relative surface energies of different crystal facets from experiment. Third, if one cleaves a crystal along a direction which does not form part of the equilibrium boundary, the crystal will spontaneously facet along those directions that do, assuming, as always, that the system is at equilibrium. Fourth, and finally, as the volume of the crystal decreases to the nanometer scale, the accuracy of the predictions one can obtain from the Wulff theorem become questionable because the energetic contribution of edges and corners at the boundary between each face becomes non-negligible.

Although the standard application of the Wulff theorem provides a means to obtain rela-

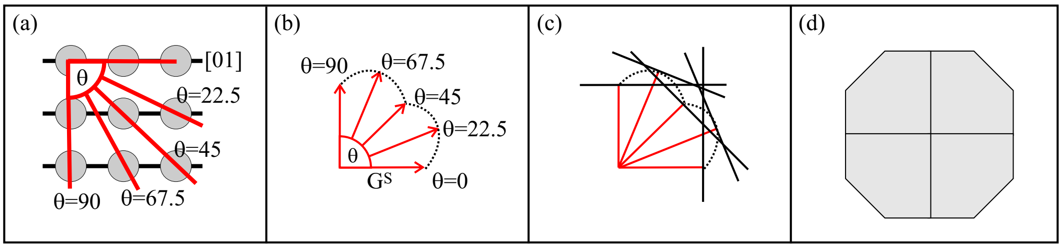


FIG. 8: (a) Schematic illustration of a 2D model crystal. Several possible cleavage planes of this crystal, labeled by the angle, Θ, that they make with the [01] symmetry plane, are indicated. (b) The first quadrant of a polar surface free energy plot for the model system sketched in (a), and assuming a correlation between the corrugation of a surface and its surface energy. For each value of Θ radial vectors are drawn from the origin of the plot with a magnitude proportional to G^S at that value of Θ, i.e., the function $G^S(\Theta)$ is plotted. (c) and (d) The Wulff planes of the polar surface energy plot sketched in (b) and the resulting equilibrium crystal shape (for all four equivalent quadrants) of the model system displayed in (a).

tive surface free energies of metals from experiment, the determination of *absolute* surface free energies is, on the other hand, notoriously difficult. This is mainly because it is a small quantity and sensitive to the presence of vacancies, adatoms, steps, and impurities. Furthermore, most experimental surface free energy measurements from which absolute surface free energies can be obtained are indirect and old, originating in the mid 1970s and before. Although in compilations of surface energies "recommended values" may be given, one would need to be brave to make a bet of any substance on the validity of a tabulated value of a surface free energy. One need only look at published results for W, for example, to see the problem: measured values range from 105 meV/Å^2 to 281 meV/Å^2 [101].

Partly because of the difficulty in acquiring reliable surface free energies of solids, when dealing with one component systems, it is common to exploit the equivalence of G^S and surface tension, γ [102]. The surface tension, particulary the surface tension of liquids, can be determined more accurately than G^S for solids. Since it is generally believed that the surface tension of a molten liquid is about 10-20 % less than G^S for the close-packed surfaces of that solid, the liquid surface tension measurements provide what is considered an *average* surface free energy of the low-index solid surfaces. Generally these values are extrapolated on "semi-theoretical" [103] grounds to 0 K, which is how most of the tabulated surface free energy values of metals are presented [46, 103].

A notable exception to the rule that experimental surface energy measurements are old are the experiments of Bonzel and co-workers on Pb in which surface free energies for *individual crystal facets* were determined from knowledge of the temperature dependence of the equilibrium crystal shapes of Pb crystallites [104]. The Pb crystallites were supported on a Ru(0001) substrate and imaged with STM at around room temperature and above, leading to the determination of the absolute free energy of Pb(111) and several other low-index orientations ((100), (110), (113), (112), and (221)). Comparison of the measured value for Pb(111), 27.5 meV/Å^2 at 323-393 K, with previous recommended values of polycrystalline Pb samples show that the new value is about 15 % smaller than the previous ones. It remains to be seen where this difference comes from and if

TABLE 3: Theoretical (DFT LDA and PBE) and experimental surface energies in meV/Å^2 for some close-packed transition metal surfaces. All data is taken from ref. [52] except for the Pb results which are from ref. [105].

	Mg(0001)	Al(111)	Ti(0001)	Cu(111)	Pd(111)	Pt(111)	Pb(111)
LDA	38.7	56.8	141.7	119.8	116.7	139.2	26.0
PBE	35.0	46.8	124.2	88.0	83.0	104.2	17.2
Exp.	49.3	71.2	124.2	114.2	125.5	155.4	27.5

the modern value is indeed superior to its predecessor. However, recent DFT (LDA) calculations tend to favor the modern result [105].

4.2.2 Theoretical Considerations of Surface Energies

In theoretical calculations, such as with DFT, the T=0 value of G^S is typically calculated, also assuming that contributions due to zero point vibrations as well as the pV term are negligible, i.e., E^S is calculated. In terms of a periodic slab calculation E^S is more conveniently defined with regard to surface area, A, as

$$G^S \sim E^S = (E_{tot}^{slab} - NE_{tot}^{bulk})/2A \quad , \tag{26}$$

where E_{tot}^{slab} is the total energy of a slab with N atoms and E_{tot}^{bulk} is the reference total energy per atom of the bulk system. The factor 1/2 takes into account the presence of two equivalent surfaces of the slab. To obtain E^s one thus needs to compute just two quantities, E_{tot}^{slab} and E_{tot}^{bulk} [106]. Before doing this one must, as always, decide on which exchange-correlation functional to trust. Unlike in the bulk, however, our comparison is limited to LDA and GGA functionals since practically nothing beyond GGA has been applied yet to real metal surfaces [107]. This is a somewhat unfortunate consequence of the fact that the post-GGA functionals, such as the meta-GGAs and hybrid functionals, are relatively new and have not yet, or have only recently, been implemented in the popular materials science DFT codes. Comparing the results of LDA and GGA (PBE) calculations for a selection of *sp* and transition metals to the 0 K experimental data proves useful and leads to the somewhat surprising result that LDA apparently outperforms GGA (Table 3). We say "apparently", of course, because the size of the error bars on the experimental values are unclear. Nonetheless in each case GGA (PBE) predicts surface energies that are about 30 % lower than LDA, and more often than not LDA is closer to experiment than GGA. This seems to be a genuine conclusion for metals since it is also true for Pb(111) for which possibly the most reliable single-crystal surface energy measurements have been made. Here LDA comes within 2 meV/Å^2 of the experimental value, whereas GGA-PBE is about 10 meV/Å^2 lower than experiment [105].

Studies on jellium surfaces provide a partial explanation for why LDA outperforms GGA for the calculation of the surface energy of metals. Specifically they show that the exchange-correlation contribution to the surface energy is calculated more reliably with the LDA due to a favorable cancelation of errors: LDA overestimates the exchange contribution to the surface energy, but underestimates the correlation contribution, whereas PBE underestimates both quantities [30, 108, 109]. Since these results on jellium surfaces are apparently transferable to real metals, it is reasonable to anticipate that functionals which are superior to LDA for jellium surfaces will also be superior to LDA for real metal surfaces. In this regard it appears that the meta-GGA TPSS, PBE-WC, and a functional from Mattsson and co-workers based on a subsystem functional approach offer some promise [26, 109, 110]. However, whether these functionals live up to expectations for real metal surfaces remains to be seen.

4.2.3 Phenomenological Theories of Surface Energies

So far we have not discussed the physics of the surface energy. Why do different metals exhibit different surface energies? Why does the surface energy of different facets of the same metal differ? Essentially both questions are the same as asking: what controls the magnitude of the surface energy? The qualitative answer to this is very simple: *the surface energy is related to the number and strength of the bonds which are broken in creating the surface.* Thus surface energies exhibit similar periodic dependencies as cohesive energies do, and surface energies are lower for more closely packed surfaces than they are for the more open ones.

(a) Surface energies and cohesive energies

For aby given element its surface energy is a fraction of its cohesive energy. Most often it turns out that for metals G^S per surface atom $\sim 1/6E^{\mathrm{coh}}$ per bulk atom [111]. This rough empirical relationship can be seen in Fig. 9(a), for example, where the ratio of experimental heat of vaporization and experimental surface energy is plotted for more than 20 metals. Correlations like this have a long history and can easily be refined to account for the elements which are outliers on the plot [112].

So where does the value of the proportionality constant come from? Simply counting the number of nearest-neighbor bonds that break in making a close-packed surface would lead one to expect a value of 1/4 or larger, since at the most closely packed (111) surface of an fcc metal 1/4 of the bonds are broken. On less closely packed surfaces obviously more bonds are broken. As discussed by Methfessel *et al.* [114, 117] the reason the simple bond cutting model fails to predict the correct proportionality constant is that it neglects to account for the variation of the bond strength with coordination number, C. In particular it must be recognized that bonds between an atom with a few neighbors are stronger than those between an atom with many neighbors. This coordination-number-bond-strength relationship is well known and has, for example, been calculated explicitly with DFT for several metals, showing that the energy per bond can be as much as twice as large for $C = 2$ compared to $C = 12$ [117, 118]. Since making an fcc (111) surface entails cutting the comparatively weak twelfth, eleventh, and tenth bonds, the overall cost to make the surface is less than would be predicted by the simple linear bond cutting concept.

The coordination-number-bond-strength relationship is qualitatively captured in simple tight binding schemes in which the energy per bond can be assumed to scale with $\sqrt{C}$ leading to

$$E^S = \frac{\sqrt{C^{bulk}} - \sqrt{C^{surf}}}{\sqrt{C^{bulk}}} E^{coh} \quad , \tag{27}$$

where C^{bulk} and C^{surf} are the coordination number of the bulk and the surface, respec-

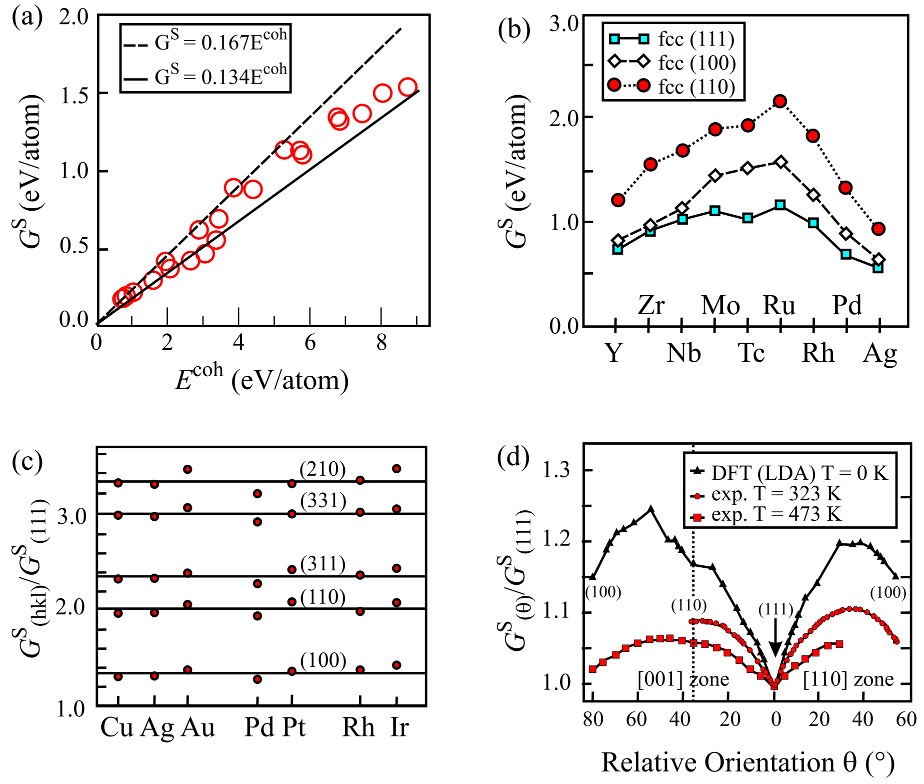


FIG. 9: (a) Plot of experimental values of the surface free energy (G^S) (from ref. [103]) against the cohesive energy (E^{coh}) (from ref. [113]) for more than twenty simple, transition, and noble metals. Lines corresponding to proportionality constants of $1/6$ and the result of eqn. (27), 0.134, are also displayed. (b) Variation of the computed DFT LDA surface energies across the $4d$ transition metal series and for various close-packed surfaces. Note that in this plot fcc crystals have been used for all metals (after ref. [114]). (c) Computed DFT anisotropy ratios, relative to the (111) surface, for the low index and the most close-packed vicinal surfaces of some noble and transition metal surfaces (after ref. [115]). (d) Plot of experimental (two lower curves) and theoretical (upper curve) anisotropy ratios, relative to the (111) surface, along the [001], [$\bar{1}$10] and [01$\bar{1}$] zones for a series of Pb surfaces (after ref. [116]).

tively. For an fcc (111) surface eq. (27) yields a surface energy per atom of $0.134E^{\text{coh}}$ which gives results rather close to the ones plotted in Fig. 9(a). Refinements of the tight binding treatment to account for repulsive forces between the atoms improves the agreement with experiment further [114, 117].

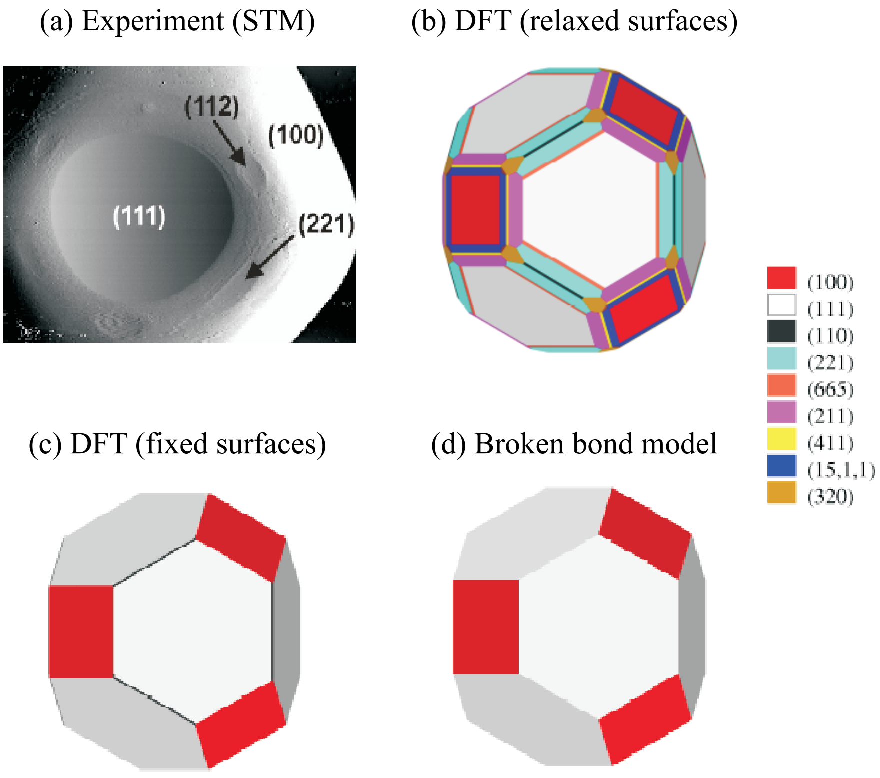
(b) Surface energy anisotropy

As we have said the variation of surface energy with the type of crystal facet exposed is known as surface energy anisotropy. Generally it is known that the surface energy of a metal is proportional to the number of broken bonds at the surface. Thus more open surfaces with more under-coordinated atoms (i.e., more broken bonds) are less stable than the close-packed ones. This effect is qualitatively seen in the equilibrium crystal shapes of metal particles which expose close-packed surfaces at the expense of more open ones. First principles theory provides a considerable body of quantitative support for this concept [105, 114–117, 119–121]. As an example we show in Fig. 9(b) the computed DFT LDA surface energies of Methfessel *et al.* [114, 117] for model fcc (111), (100) and (110) surfaces of the $4d$ transition metals. Clearly for each metal the surface energy increases along with the corrugation of the surface, being lowest for the (111) surfaces and highest for the (110) surfaces.

More recently Galanakis *et al.* [115, 120] have shown that for the surfaces of several fcc metals there is an almost perfect linear correlation between the *relative surface energies* of different crystal facets and the number of broken bonds. This is shown in Fig. 9(c) for a number of fcc transition metal surfaces. Precisely the DFT LDA computed anisotropy ratios (relative to the (111) surface) for the (100), (110), (311), (331), and (210) surfaces of several transition metals are displayed. The solid horizontal lines are the ideal broken-bond ratios, which for the (100) surface, for example, is 4/3 since each atom on this surface has only 8 nearest neighbors compared to 9 in the (111) surface. It can be seen that in every case the computed results fall on the ideal lines or within a few percent of them. Calculations on other fcc metal surfaces, including an extensive series of 35 Pb surfaces and a large set of Cu surfaces predict that this trend also applies to these substrates; typically computed surface energies were within 5 % of what would be predicted from the broken bond rule [116, 121]. It has been argued that the linear correlation in the *relative* surface energies is not inconsistent with eqn. (27) and the basic knowledge that the binding energy does not scale linearly with coordination number C, by recalling that the square root in eqn. (27) can be linearized in the regime of high coordination [115].

Recent experimental results on Pb crystallites [104, 123, 124], provide valuable data with which to assess the validity of the trends predicted by DFT. Summarizing an extensive series of comparisons between experimental and DFT results [105, 116, 122, 125], it is found that the surface energy anisotropies obtained from experiment and predicted by theory agree with each other reasonably well. In Fig. 9(d), for example, the experimental and theoretical surface energy anisotropies are plotted along the [001], $[\bar{1}10]$ and $[01\bar{1}]$ zones. At 323 and 473 K the experimental anisotropies are 11 and 6 %, respectively, whereas the T = 0 K theoretical anisotropy is at 25 %, expectedly higher than the finite temperature experimental values. In addition the directions of the maxima and minima of the theoretical anisotropy curve coincide with the experimental values. Moreover, when the theoretical equilibrium crystal shape - obtained by performing a Wulff construction with the theoretical surface energies - is compared to experiment, the qualitative agreement is good. As shown in Figs. 10(a)-(b) many features of the experimental equilibrium crystal shape are reproduced by the theoretical one, such as the 3-fold symmetry of the central (111) facet and the smaller peripheral (211) and (221) facets. Also shown in Figs. 10 are the predicted equilibrium crystal shapes obtained from the surface energies of unrelaxed Pb surfaces (Fig. 10(c)) and from the application of the linear broken bond rule. It is clear that the equilibrium crystal shapes obtained with the alternative data sets differ noticeably from experiment. In particular the assumption of a linear dependence of the surface energy with the number of broken bonds results in an incorrect crystal shape with just the low-index (111) and (100) surfaces present. Thus although approximate linear correlations are observed between the surface energy and the number of broken bonds the deviations from linearity are essential for a correct description of the equilibrium crystal shape.

4.3 Surface Electronic Structure


(a) Experiment (STM)

(b) DFT (relaxed surfaces)

(c) DFT (fixed surfaces)

(d) Broken bond model

FIG. 10: (a) Scanning tunneling microscopy (STM) image of part of a Pb crystallite showing the (111) and the surrounding 2-fold symmetric (221) and (211) facets as well as a (100) facet at the contact edge to the substrate. The image size is *ca.* 970 × 750 nm. (b)-(d) Three dimensional equilibrium crystal shapes of Pb constructed from DFT LDA surface energies. (b) is obtained from computed surface energies on relaxed surfaces, (c) from computed surface energies on fixed surfaces, and (d) with the vicinal surface energies obtained from the linear broken bond model (after ref. [122]).

Let's now consider how the electronic structure at the surface differs from that in the bulk. We will see that the loss of translational symmetry along the surface normal has important and interesting consequences for the electronic structure. As before we first look at the surfaces of simple metals, where we find that again jellium provides useful insight, we then move on to the transition metals and tight binding arguments. We close with a brief discussion of surface states.

4.3.1 Jellium Surfaces: Electron overspill; Surface Dipole; and Φ

Some of the most important understanding of surface electronic structures comes from the early studies of Lang and Kohn on jellium surfaces [126, 127]. A discussion of the key findings of their studies proves a useful way to introduce important concepts such as the surface dipole and the work function.

Take the jellium model that we introduced earlier for the infinite crystal and terminate the positive background (n_+) abruptly along a plane at $z = 0$, with the positive uniform

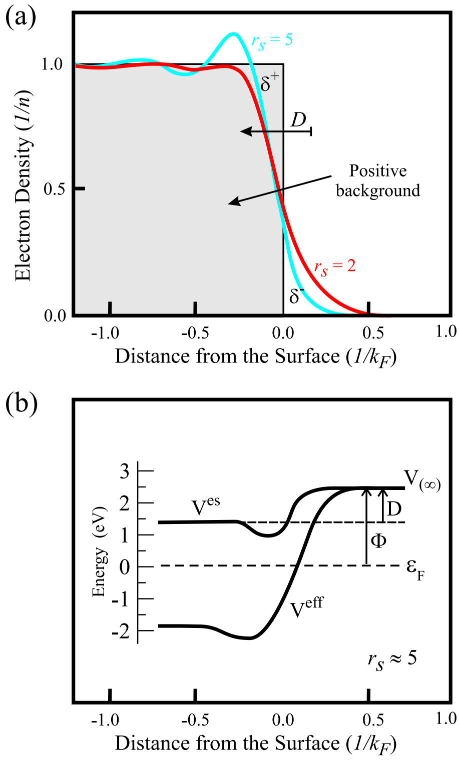


FIG. 11: (a) Self-consistent electron density distributions at a jellium surface for r_s=2 and r_s=5. (b) Schematic illustration of the potentials that develop at the jellium surface within the local density approximation for an $r_s \sim 5$. All symbols are defined in the text (after ref. [126]).

background now filling the half-space $z \leq 0$ with the form:

$$\begin{aligned} n_+(z) &= \overline{n}, z \leq 0 \\ &= 0, z > 0 \end{aligned} \tag{28}$$

where $\overline{n}$ is the mean density of the positive charge in the ionic lattice. For a range of densities ($r_s = 2 - 6$) Lang and Kohn considered how the density (within the LDA) would behave at such an interface. The now famous plot displayed in Fig. 11(a) was obtained, which shows that: (i) the electron density spills into the vacuum; and (ii) the density within the boundary oscillates in a Friedel manner with an amplitude that decreases asymptotically with the square of the distance from the surface. The characteristic wavelength is one half of the Fermi wavelength, k_F, where $k_F = (3\pi^2 n)^{1/3}$ [128]. The amount of overspill into the vacuum and the amplitude of the Friedel oscillations depends on r_s. The smaller r_s is, the larger the overspill. The larger r_s is, the greater the amplitude of the oscillations.

The potentials associated with such density distributions are sketched in Fig. 11(b). In particular the total effective (Kohn-Sham) potential, $V^{\rm eff}$, and the electrostatic potential, $V^{\rm es}$ are plotted. The difference between them is the exchange-correlation contribution to the total effective potential which one can see comprises the largest part of $V^{\rm eff}$. This is generally true for low and intermediate densities. Two aspects of the potentials are worth commenting upon. First, as a result of the local-density approximation, V^{eff} vanishes exponentially into the vacuum. This asymptotic behavior is not correct. Instead, since as an electron moves out of a metal surface its exchange-correlation hole stays behind, flattening out on the surface, the effective potential should follow an image-like form:

$$V^{\mathrm{eff}}(z) \sim \frac{1}{4|z - z_{image}|} \quad . \tag{29}$$

Here z_{image} is the so-called image plane, which for many purposes is considered the "effective surface plane" [96, 129]. For typical values of r_s the image plane (from LDA predictions) of clean jellium surfaces resides about 2-3 Å to the vacuum side of the positive uniform background ($z = 0$) [129]. As we will see, however, the LDA error in the asymptotic behavior of V^{eff} has little effect on the properties of interest here such as the ground-state electron density and work function which are determined largely by the position and height of the potential rather than its detailed shape.

The second feature of the potentials sketched in Fig. 11(b) that we comment upon is V^{es}, the electrostatic potential. Although V^{es} is a relatively small component of the barrier, it is of the utmost importance since it is closely related to the work function, Φ. V^{es} arises because the spread of electrons beyond the edge of the positive background renders the electrostatic potential in the vacuum, $V^{es}(\infty)$, higher than that in the metal interior, $V^{es}(-\infty)$. Thus an electron trying to leave the metal encounters an electrostatic surface dipole layer, D, with a electrostatic potential energy difference of height

$$D = V^{es}(\infty) - V^{es}(-\infty) \quad . \tag{30}$$

From Poisson's equation this can be written as

$$D = 4\pi \int_{-\infty}^{\infty} z[n(z) - n_{+}(z)]dz \quad . \tag{31}$$

This integral across the surface boundary is obviously an electric dipole, the surface dipole, which is related to Φ through

$$\Phi = D - \mu \quad , \tag{32}$$

where μ is the electron chemical potential, which in a metal at 0 K is equal to the Fermi level (as discussed in section 2). Thus we arrive at the definition of the work function as the minimum work necessary to remove an electron from a metal at 0 K [130].

Clearly the more the electrons spill into the vacuum, the larger D is. Indeed Φ generally increases with decreasing r_s as is illustrated by Fig. 12(a) where the work function of jellium is plotted as a function of r_s along with several experimental values for polycrystalline metals. It can also be seen from the plot that the trend predicted by jellium is indeed observed with experimental measurements on real crystals. Moreover, the absolute values of Φ predicted with the jellium model fall in the range 2-4 eV and come within 10-20 % of experiment for each of the *sp* metals listed.

A similar reasoning, although with the necessary introduction of a crystal lattice, explains the well-established fact that for real crystals, Φ can differ from one facet to the other, a concept known as work function anisotropy. For example, the measured values of Φ for the (111), (100), and (110) surfaces of Cu are 4.74, 4.64, and 4.52 eV, respectively [46].

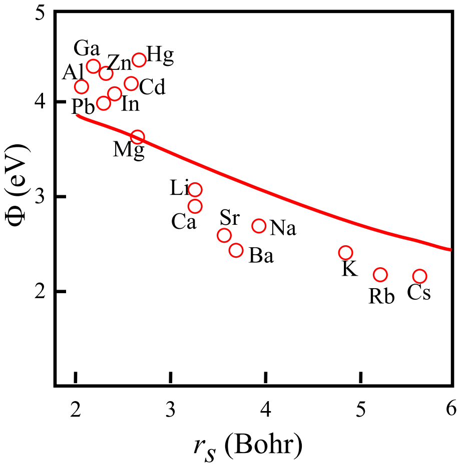


FIG. 12: Computed work function of jellium as a function of r_s along with measured experimental values for polycrystalline surfaces (after ref. [127]).

Since μ or E_F in eqn. (32) is a bulk quantity the anisotropy in Φ comes directly from the different dipoles established at the different surfaces. Generally it is known that the more open a surface, the smaller D is and consequently the smaller Φ is, as we see for Cu above. Obviously, for jellium D is the same for all surface orientations. However, for a real crystal, say fcc, the electron density is quite smooth at the (111) surface getting more corrugated at the more open surfaces. In the latter situations the electron density will smoothen out parallel to the surface to lower the kinetic energy, and as a consequence the surface dipole moment will be reduced compared to that of the closer packed surfaces.

4.3.2 Transition Metal Surfaces: Band Narrowing and Surface Core Level Shifts

As we know tight binding arguments are more appropriate than jellium when seeking to gain qualitative insight of transition metal surfaces. In tight binding language the surface suppresses a certain number of hopping integrals, since the surface atoms have lost some neighbors in any sphere of coordination. This reduces the average width of the PDOS on a surface atom relative to the bulk. Such "band narrowing" is a general phenomena of solid surfaces when the valence states are comprised of localized orbitals such as the d valence orbitals of the transition metals. The bands of the surface atoms cannot narrow without consequence, however. Given that the whole metal has a single Fermi level, narrowing alone would lead to an unrealistic lack or surplus of electronic charge on the surface atoms depending on the filling of the band. To avoid (or to at least reduce) this the center of gravity of the narrowed bands shift; either up or down in energy. The magnitude and direction of the shift, Δ_S, can be approximated with the rectangular d band model introduced earlier, and is given by,

$$\Delta_S = E_F(1 - \sqrt{\frac{C_{surf}}{C_{bulk}}}) \quad , \tag{33}$$

where, as before, C_{bulk} and C_{surf} are the coordination numbers of atoms in the bulk and at the surface, respectively. The energy zero in eq. (33) is the center of the bulk d band, E_d, and thus within this simplified model Δ_S is negative for less than 1/2 filled bands,

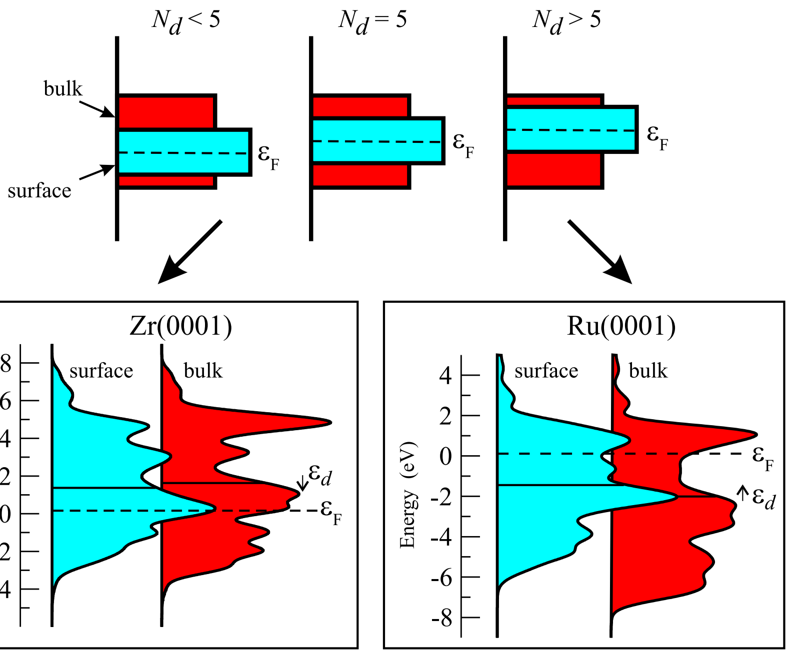


FIG. 13: Upper part: schematic illustration of d-band narrowing at transition metal surfaces and its consequence for the energy levels of the surface atoms with less than 5 d electrons ($N_d < 5$), exactly 5 d electrons ($N_d = 5$), and more than 5 d electrons ($N_d > 5$). Lower part: PDOS for the d orbitals in bulk Zr and Ru and at the surface of Zr(0001) and Ru(0001), as computed from a plane-wave pseudopotential DFT calculation within the LDA. E_d is the center of gravity of the d PDOS and the small arrows indicate that E_d is lower at the surface than in the bulk for Zr whereas E_d is higher at the surface than in the bulk for Ru (computed by the authors).

positive for more than 1/2 filled bands, and zero for an exactly half filled band. We illustrate schematically the essence of this model in the upper part of Fig. 13. It is also worth pointing out that since Δ_S increases with the number of broken bonds at the surface, the more open the surface, the larger the shift, and naturally as one descends into the bulk of the crystal the bulk value for the band width is immediately recovered (within the model).

The qualitative behavior predicted from the rectangular d band model can actually be seen in self-consistent DFT calculations, where the shape of the DOS is explicitly calculated. For example, we show this in the lower part of Fig. 13 where the bulk and surface PDOS projected on to the valence d orbitals is plotted for bulk Zr and Ru and for Zr and Ru (0001) surfaces. For both Zr and Ru the d PDOS associated with the surface atoms is narrower than that of the bulk. For Zr with < 5 d electrons the surface d PDOS moves down in energy (~ 0.1 eV) relative to the bulk, and for Ru with > 5 electrons the surface d PDOS moves up in energy (~ 0.3 eV) [131].

Of more significance, perhaps, is that the shifts in the valence levels correlate with shifts in the core electrons and that the latter are now accurately and routinely measured with x-ray absorption spectroscopy (XPS) [65, 132, 133]. Such shifts in the core electrons, known as surface core level shifts (SCLS), have been measured on many close-packed transition metal surfaces finding the same qualitative trend illustrated in Fig. 13 for the valence states, i.e., a shift to deeper binding energies is observed for elements to the left of the transition series and a shift to shallower binding energies for elements to the right. See, for example, refs. [132, 134, 135]. Surface core level shifts can also be computed within the framework of DFT. However, to ensure good agreement with experiment it is often necessary to put in a little more effort with the DFT calculation than simply computing the differences in the eigenvalues of core electrons at the surface and in the bulk, as was done for the valence DOS (Fig. 13). Consider what is actually measured in a core-level photoemission experiment: it is the difference in the energy it takes to remove a core electron from an atom at the surface and from an atom in the bulk. From this definition it follows directly that the SCLS of a particular core level is the difference in the total energy between a sample with a core hole at the surface compared to the core hole being in a bulk atom. This binding energy shift thus includes changes in the core orbital energies between bulk and surface atoms *and* differences in the screening of the core hole created by the different surroundings of the core hole at the surface and in the bulk of the material. The former effect is typically called the "initial state" contribution, whereas the latter is called the "final" state contribution. The inclusion of such "final state" effects can often be necessary if quantitative agreement between experimental and theoretical values of SCLS is sought [135–138].

4.3.3 Surface States

As we have seen the electronic structure of metal surfaces is likely to differ from that in the bulk. One way this altered behavior is exemplified is through the formation of so-called surface states [139–142]. Surface states represent interesting physical phenomena in their own right, as examples of confined two-dimensional electronic systems, but can also affect the physical and chemical properties of metallic interfaces, playing, for example, a role in the mediation of adsorbate lateral interactions [143–145]. They are routinely observed in experiment, notably with angle-resolved photoemission spectroscopy (ARPES) or with scanning tunnelling microscopy when they scatter from surface defects or adsorbates [146, 147].

Consider a wavefunction in the bulk as it approaches a metal surface. If it is reflected back into the bulk and decays exponentially into the vacuum it is a bulk state (Fig. 14(a)). Certain bulk states may have a larger weight at the surface than in the bulk. Generally these are referred to as surface resonances (Fig. 14(b)). However, other wavefunctions may be localized almost exclusively at the surface and decay exponentially into the bulk as well as into the vacuum (Fig. 14(c)). These electronic states localized near the surface are surface states, and can be defined more precisely as states that occur in "forbidden" [148] regions of the bulk band structure, i.e., at an energy and $k_{\|}$ value or point-group symmetry for which there are no bulk states into which they can decay. This implies that surface states appear in "gaps" of the bulk band structure. Even though metals do not (by definition) exhibit *absolute* band gaps there can be many regions of $\boldsymbol{k}$-space for which at specific energies there are no states. For example, in the bulk band structure of Cu (Fig. 2(a)) there are no states above the d band until well above E_F along the path $\Gamma \rightarrow L$. Thus this represents a potential region in which, given the appropriate conditions, a surface state may appear. Indeed the (111) surface of Cu is perpendicular to the $\Gamma \rightarrow L$ path and, as we will see, a surface state does indeed reside in this region of the surface projected bulk band structure of Cu(111).

Surface states are usually classified as Shockley [148] and Tamm states [149], and we now

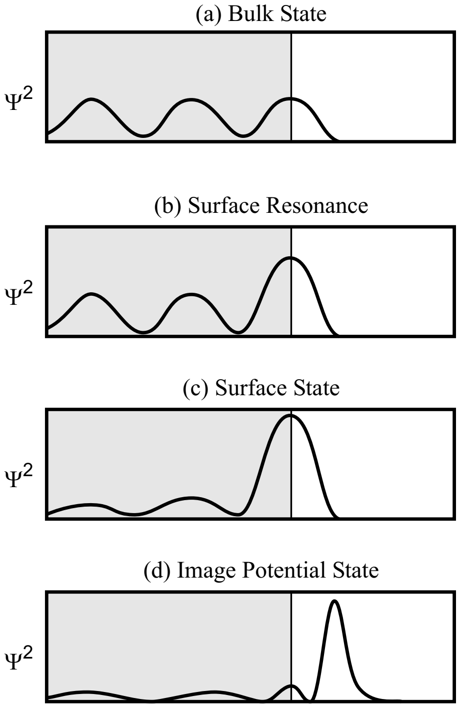


FIG. 14: Schematic illustration of: (a) an idealized bulk state; (b) an idealized surface resonance; (c) an idealized surface state; and (d) an idealized image potential state.

briefly discuss these two types of surface state in turn. However, we caution in advance that while useful the distinction is somewhat arbitrary since both types of state describe the same physical phenomenon of a wavefunction that is localized at the surface and decays exponentially into the bulk.

(a) *Shockley states:* These are typical of the simple and noble metals. Indeed the hexagaonal close-packed surfaces of Be, Mg, Al, Cu, Ag, and Au all possess an occupied Shockley state [150]. They arise simply because the presence of the surface allows solutions of the Schrödinger equation which would otherwise be imaginary in the bulk to become real in the semi-infinite crystal. Shockley states appear close to the low energy (i.e., high binding energy) border of a gap and reveal a free-electron-like behavior parallel to the surface. A particularly well characterized Shockley state is the one that occurs on Cu(111). According to ARPES this is a free electron-like state which at the $\overline{\Gamma}$ point of the surface Brillouin zone resides $\sim$ 0.4 eV below E_F [151, 152]. DFT calculations agree with this finding, as can be seen from the computed band structure of Cu(111) shown in Fig. 15. The Shockley state can be seen at the $\overline{\Gamma}$ point just below E_F.

(b) *Tamm states:* These are characteristic of more tightly bound systems such as the transition metals in which the valence electrons are d states. Tamm states are split-off states due to the reduced atomic coordination of the surface and the weaker potential that arises (which was discussed in section 4.3.2). They reside also at the low energy border of gaps and often exhibit negative effective masses. Noble metal surfaces such as Cu(111) also exhibit Tamm states (in addition to Shockley states) and indeed in Fig. 15 an occupied Tamm state 1.8 eV below E_F can be seen at the $\overline{M}$ point split off from

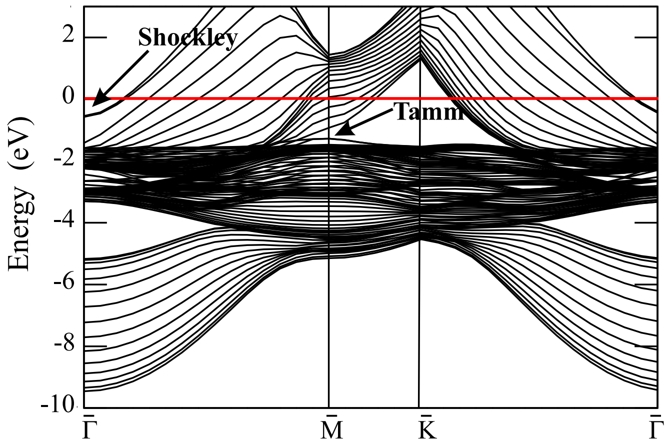


FIG. 15: Surface projected bulk band structure for a 12 layer Cu(111) slab as computed from a plane-wave pseudopotential DFT calculation within the LDA (computed by the authors).

the top of the Cu *d* band. Again the computed value of this surface state agrees with experiment [153, 154].

Finally we mention yet one more type of state that can occur at metal surfaces, these are so-called image potential states which are localized mostly in the vacuum region of the metal surface (Fig. 14(d)). Recall from section 4.3.1 how the image potential rises to the vacuum level V_∞ as one moves out from the surface into the vacuum (Fig. 11(b)). This potential can actually support *unoccupied* bound states, i.e., image potential states. These states lie above the Fermi energy, in a Rydberg-like series of states converging towards the vacuum level. Should such image potential states become populated with electrons these states can have relatively long lifetimes. The reader interested in learning more about image potential states, in particular, and surface states, in general, should consult the book by Davison and M. Stęślicka [139] or some of the excellent reviews on these topics [142, 155, 156].

5. Conclusions and Perspectives

Much is known about clean metal surfaces. In many cases we know where the atoms are, where the electrons are, and how stable both the atoms and electrons are at their chosen locations. We have seen how at some metal surfaces the atoms rearrange to form complex structures not known elsewhere in nature, whereas at other metal surfaces the atoms remain happily at their bulk-like positions. We have seen how electrons literally spill out of some metal surfaces, whilst at others they become trapped finding it almost impossible to escape. We have seen how at some metal surfaces the electrons signal their knowledge of the surface by moving up in energy, at others they move down, and at yet other metal surfaces they do nothing, apparently oblivious to their reduced coordination compared to the bulk. And, we have seen that the cost in energy to make some metal surfaces is high, to make others it is low, and the balance between them conspires to yield a rich variety of equilibrium shapes for metal crystals. This body of knowledge comes from countless surface science experiments over the last 30-40 years, a small few of which we have mentioned, and from theoretical calculations, a larger number of which we have mentioned. In particular, we have focused mainly on the contributions from density-functional theory, although the qualitative insight obtained from simplified tight-binding schemes should not be overlooked [48, 157].

Let's now recap some of the key points made already and outline a few challenges and issues that remain to be addressed.

(a) *Surface structures:* Atoms at clean metal surfaces generally do not maintain their bulk-truncated positions. Relatively simple *relaxations* in which the interlayer spacings in the surface region are modified are common, as are more complex *reconstructions* in which the atoms in the surface region undergo lateral displacements or experience a change in atomic density.

In most cases the results of DFT calculations and LEED analyses agree on the structural details of a particular relaxation or reconstruction. Further, DFT can generally provide an adequate *a posteriori* explanation for why a relaxation or reconstruction take places, such as for the hex phase of the late $5d$ fcc transition metals. However, there are several surfaces where the results of LEED analysis and DFT calculations still disagree, notably the close-packed hexagonal surfaces of Ru and Rh. Such discrepancies deserve further attention and their resolution provides a challenge for experiment and theory alike.

(b) *Surface energetics:* The most fundamental energetic quantity of a surface is the Gibbs surface free energy. This controls the surface that forms under conditions of constant temperature and pressure. Periodic trends in the Gibbs surface free energy have been discussed, as have variations across different types of metal surface. The statement that the surface energy is proportional to the number and strength of the bonds which are broken in creating the surface has been shown to be qualitatively correct.

Demonstrably reliable and quantitatively correct experimental surface energies for metals are however generally lacking. The recent STM-based experiments for Pb are a welcome development. There is a pressing need for more measurements of this kind.

The lack of reliable surface energies for specific crystal facets of metals makes it difficult to evaluate the performance of DFT in computing surface energies. More displeasing, however, is the conclusion that an exchange-correlation functional superior to LDA for the calculation of surface energies of real metals has yet to be identified. Based on insight gleaned from jellium surfaces it appears that progress in this regard can be expected soon. However, an important word of caution on this issue is necessary. As we said in the introduction, one is typically interested in clean metal surfaces as a prelude to understanding how they interact with their environment. One may, for example, be interested in the adsorption of atoms and molecules at a surface or the formation of steps, kinks, and vacancies. A functional that performs well for the surface energy is only of real value if it accurately computes these other properties too.

(c) *Surface electronic structures:* The general qualitative behavior of the ground-state electronic structure at metal surfaces is qualitatively well understood. Much of this insight comes from the pioneering studies of Lang and Kohn on jellium surfaces and the semi-empirical tight-binding studies discussed briefly here and covered in more detail elsewhere [48]. The former provide the basis for understanding the physical origin of the work function and trends in the work function from one metal to another. Whereas the latter are helpful for understanding concepts such as band narrowing and surface core level shifts.

Further Reading

Aside from the many original articles, review papers, and books cited already, the interested reader may wish to consult the following texts for complimentary and in some cases more detailed discussions on the physical and chemical properties of metal surfaces:

- *Physics at Surfaces* by A. Zangwill: The first half of this book deals exclusively with clean solid surfaces, with a large chunk of this devoted to metal surfaces. It is positioned at a somewhat similar level to the present article.
- *Theoretical Surface Science; A Microscopic Perspective* by A Gross: The most up to date of the books in this area, with detailed discussions of modern electronic theories and their application to metal (and other) surfaces.
- *Concepts in Surface Physics* by M.C. Desjonquères and D. Spanjaard: Provides a very detailed discussion of many aspects of the electronic structures of metals, in particular the basis and application of tight-binding methodologies.
- *Interactions of Atoms and Molecules with Solid Surfaces* edited by V. Bortolani, N. H. March, and M. P. Tosi: Although somewhat out of date Chapter 5 by J. E. Inglesfield is excellent, and well worth a read.
- *Theory of the Inhomogeneous Electron Gas* edited by S. Lundqvist and N. H. March: Chapter 5 by N. D. Lang is a good "one stop shop" for most of the early material stemming from the work of Lang and Kohn.

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[2] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1994).
[3] In practise, if the system has a net magnetic moment, one may need to perform spin-density functional theory calculations which is a function of 6 variables.
[4] L. H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1927).
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[6] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).
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[8] More precisely the second theorem of Hohenberg and Kohn tells us that the ground state electron density can be calculated, in principle exactly, using the variational method involving only the electron density,

$$E_0 = E[n_0] \leq E[n] \quad ,$$

i.e., upon variation, the energy functional, $E[n]$, assumes its minimum value for the ground-state electron density n_0.

[9] W. Kohn and L. Sham, Phys. Rev. Lett **140**, 1133 (1965).

[10] This may also be called "Pauli correlation" because it correlates the dynamics of electrons of like spin. Obviously electrons also repel each other because of their charge.

[11] A distinction between "empirical" and "non-empirical" DFT functionals is also common. Empirical in this context covers those functionals that are designed in order to reproduce experimental results or the results of high-level quantum chemical calculations for quantities such as atomization energies and bond lengths. Typically "training sets" comprised of a large number of well defined energies and structures of small gas phase molecules are used when making this comparison. The other essentially opposing, non-empirical, strategy is to design functionals that abide by a number of well-known physical constraints which the exact E^{xc} functional should obey and do not include parameters other than fundamental constants.

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[17] A note on the nomenclature behind DFT functionals may be appropriate. Functionals are most often named after their authors' in such a way that the name "PBE" comes from a paper by Perdew, Burke, and Ernzerhof. Occasionally the year the paper was published is appended. And if the functional is one of the so-called hydrid functionals, discussed in section 2.2(c) it is common to add the number of parameters used when mixing the Hartree-Fock exchange with the DFT exchange and correlatincorrelation. For example, PBE0, is a hybrid functional with zero mixing parameters.

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[23] PBE and its off-spring differ only in how they treat electron exchange. The exchange component of GGA-PBE is

$$E_x^{PBE}[n] = \int n\epsilon^{\mathrm{xc-unif}}\left(n(\mathbf{r})\right) F_x^{PBE}(n, \nabla n(\mathbf{r}))\, d^3\mathbf{r}$$

where F_x^{PBE} is an exchange enhancement factor given by

$$F_x^{PBE}[n, \nabla n(\mathbf{r})] = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}$$

with the dimensionless reduced gradient, $s = |\nabla n|/2n(3\pi^2 n)^{1/3}$. In the original PBE $\kappa = 0.804$. In revPBE $\kappa = 1.245$. In RPBE $F_x[n, \nabla n(r)] = 1 + \kappa - \kappa exp(-\mu s^2/\kappa)$, and in PBE-WC μs^2 takes a more complex form.

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[28] The philosophy behind the hybrid functionals is simple and rooted in the adiabatic connection formula, which is a rigorous *ab initio* formula for the exchange-correlation energy of DFT. One convenient expression of this formula is:

$$E^{xc} = \int_0^1 U_{xc}^{\lambda} d\lambda \quad ,$$

where λ is an interelectronic coupling strength parameter that switches on the $(1/r_{ij})$ Coulomb repulsion between electrons and U_{xc}^{λ} is the potential energy of exchange and correlation at λ. This formula connects the non-interacting reference system with the fully interacting one all at density n. Recognizing that the non-interacting $\lambda = 0$ limit is nothing more than HF exchange, it is expected that exact exchange must play a role in "better" exchange-correlation functionals and thus DFT exchange and correlation functionals are mixed with a fraction of HF exchange.

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[54] It has been argued that the problem with cohesive energies computed with PBE0 is that the energy of the isolated atoms is badly described [51]. For many other properties, such as adsorption on metals or the size of band gaps in semi-conductors and insulators PBE0 (and hybrid functionals in general) can offer considerably improved performance over LDA, GGAs, and meta-GGAs [51, 57, 158].

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such as basis set, treatment of core electrons, integration over $\boldsymbol{k}$ space, the calculation of the reference bulk atom, the slab thickness, and the slab relaxation must be very carefully checked. See ref. [52] for a more detailed discussion on what is necessary to insure that numerically well-converged values of E^S are computed.

[107] To the best of our knowledge the only theoretical report of a surface energy computed with something beyond GGA is Fiolhais and Almeida [162]. In that paper results for the meta-GGA ("PKZB") are reported as well as results for LDA, PBE, and BLYP for a number of simple metal surfaces.

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[131] Of course, when one looks more closely at the details of the self-consistent electronic structures obtained from the DFT calculations one finds that the actual details of the electronic redistribution are somewhat more complex than the simple model would suggest. Effects such as *sp* to *d* electron charge transfer and electron flow into the vacuum also play a role, but these will not be discussed here. See ref. [165], for example, for more details.

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