

# Calculation for Energy of (111) Surfaces of Palladium in Tight Binding Model

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## ABSTRACT

In this work calculation of energetics of transition metal surfaces is presented. The tight-binding model is employed in order to calculate the energetics. The tight-binding basis set is limited to d orbitals which are valid for elements at the end of transition metals series. In our analysis we concentrated on electronic effects at temperature  $T=0$  K, this means that no entropic term will be presented and since we study unrelaxed structures, no elastic deformation contribution will be present either. Density of states is calculated for atoms at the surface and in the bulk for palladium by using the recursion method, when the potential includes only first and second nearest neighbor interactions. The surface energy of fcc (111) surfaces of Pd is also calculated.

## KEYWORDS

Local Density of States, Tight binding Model, Surface Energy, Recursion Method

## 1. INTRODUCTION

The study of energetics of surfaces is of prime interest for the understanding of various processes such as crystal growth, surface morphology, or roughening transition. Phenomenological study of metal surfaces is presently thus of interest in the science and technology. The study of these surfaces is presently the subject of intensive investigations since they may provide an appropriate substrate for growing nanostructures [1,2]. It is well known that the energetic properties of steps are fundamental in understanding epitaxial growth, surface, roughening transition and equilibrium crystallite shapes. Calculation the energy of flat surfaces of metals is thus of interest either since it is essential for calculation the energy of vicinal surfaces. Furthermore, steps have been shown to modify the adatom motion at surfaces It is thus of importance also for understanding diffusion at surfaces to chart the energetics of steps.

For technological applications in relation to the use of surface properties, the understanding and control of roughness and instabilities phenomena for pure metal and alloy crystal surfaces is a prerequisite. Due to the very low symmetry of these systems, first-principle

calculations are scarce and limited to a very small number of geometries and metals, for instance Al [3,4], Cu [5], Pt [6]. On the contrary many theoretical works have been based on semi-empirical potentials like embedded atom model (EAM) [7,8], Sutton–Chen potential [9] or effective medium theory (EMT) [10]. In another approach Vitos et al. [11] have derived step and kink energies of most transition metals from effective pair potentials (EPP) deduced from a first-principle data base of surface energies.

More recently, Mehl and Papaconstantopoulos [12] have proposed a very attractive method to determine the tight-binding parameters at each atomic distance. The aim of this paper is, on the one hand, to show that by using a non-orthogonal basis set of pure d-band, calculation of surface energy is also possible and it is in agreement with experiments.

The paper is organized as follows. In Sec. 2, the tight-binding model used for calculating total energies of transition metals is presented. The model is made explicit for application on fcc(111) surfaces. In Sec. 3, numerical results for density of state and local density of state of Pd are presented and discussed in detail. In Sec. 4 result for surface energy of fcc(111) of Pd are presented and

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compared with other methods Finally, conclusions and a summary are presented in Sec. 5.

## 2. MODEL

Our aim is to compute the total energies of different crystal configurations in order to compare them. In a tight-binding (TB) Model, the crystal energy is usually expressed as being composed of an attractive and a repulsive part.

$$E_{coh}(R) = E_{band}(R) + E_{rep}(R) \quad (1)$$

Where  $E_{band}$  is due to the broadening of valence electronic levels into a band and  $E_{rep}$  would be any other effect, notably the ion-ion repulsion. The repulsive energy will be described by a Born-Mayer pair wise potential limited to first nearest neighbor.

Since we are interested in computing band energies for transition metals, we use a tight-binding scheme where only the d electrons are taken into account. It has been shown [13] that, at least for transition metals not too close to the extremes of the transition-metal series, the cohesive properties are by far dominated by the valence d electrons. The bulk band energy is written as:

$$E_{band} = \int_{-\infty}^{E_F} EN(E)dE \quad (2)$$

Where  $N(E)$  is the total density of states and  $E_F$  is the Fermi energy of the system. The zero energy is chosen to be at the center of gravity of  $N(E)$ . When our system deviates from a bulk crystal, i.e., we deal with impurities, surfaces, etc., it is convenient to introduce the notion of local density of states (LDOS), which will be defined more precisely in the following. To each atomic site  $i$ , we assign a local density of states  $n_i(E)$ . For an atom at a site different from the bulk, the LDOS will be perturbed compared to a bulk atom:  $n_i(E) = n(E) + \delta n_i(E)$

Where  $n(E)$  is the bulk density of states per atom and  $\delta n_i(E)$  is the LDOS perturbation. The perturbation  $\delta n_i(E)$  causes a perturbation  $\delta V_i$  of the potential at site  $i$ . Both perturbations are interdependent and should be calculated self-consistently. However, in metals, screening of charge takes place within an interatomic distance and the change of the potentials  $\delta V_i$  may be obtained by requiring local charge neutrality [14]. The band energy becomes:

$$\delta E_{band} = 2 \sum_i \left[ \int_{-\infty}^{E_F} E \delta n_i(E, \delta V_1, \dots, \delta V_j, \dots) dE - N_i \delta V_i \right] \quad (3)$$

Where  $N_i$  is the number of d electrons at site  $i$  and the second term in the brackets avoids the double counting of the change in electron-electron interactions responsible for the shift  $\delta V_i$  [14] The density of states of a system is calculated using a tight-binding Hamiltonian  $H_{TB}$ . It is

assumed that the set of d orbitals,  $\Phi_{i\lambda}$  ( $\lambda = xy, yz, zx, x^2+y^2, 3z^2-r^2$ ) centered at all sites  $i$ , provides a complete orthonormal basis on which we can expand the electronic wave functions  $\psi_n$  of energy  $E_n$ . The matrix elements of the Hamiltonian in this basis will be determined by the hopping integrals  $\langle \varphi_{i\lambda} | V_i | \varphi_{j\mu} \rangle$ , usually limited to nearest neighbors.

The hopping integrals are completely determined by three hopping parameters ( $dd\sigma, dd\pi, dd\delta$ ) and the direction cosines of the vector  $R_{ij}$  connecting sites  $i$  and  $j$ .

The variation of these parameters with distance is taken to be exponential. The local density of states of a given atom is defined using the Green operator:

$$G(z) = \frac{1}{z - H_{TB}} \quad (4)$$

$$n_i(E) = 2 \sum_{\lambda} -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} \langle i\lambda | G(E + i\epsilon) | i\lambda \rangle \quad (5)$$

$$= 2 \sum_{\lambda} -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} G_{ii}^{\lambda\lambda}(E + i\epsilon) \quad (6)$$

$$= 2 \sum_{n,\lambda} |\langle \varphi_{i\lambda} | \psi_n \rangle|^2 \delta(E - E_n) \quad (7)$$

The quantity  $G_{ii}$  can be expanded as a continued fraction [14].

$$G_{ii}^{\lambda\lambda}(z) = \frac{1}{z - a_1^{i\lambda} - \frac{b_1^{i\lambda}}{z - a_2^{i\lambda} - \frac{b_2^{i\lambda}}{\ddots \frac{z - a_N^{i\lambda} - b_N^{i\lambda}}{\sum z}}}}$$

In order to calculate  $G_{ii}^{\lambda\lambda}(z)$  at first coefficients of expansion  $b_j^{i\lambda}$  and  $a_j^{i\lambda}$  should be calculated.

When the corresponding coefficients are exact up to the level  $n$ , the LDOS has  $2n$  exact moments. The more accurate a calculation is required to be, the more exact moments need to be included:

$$\mu_p^i = \int_{-\infty}^{E_F} E^p n_i(E) dE \quad (8)$$

In this work, the LDOS of an atom in a system is evaluated by calculating exactly 12 first levels in a recursion scheme and replacing the remaining part of the continued fraction by the square-root terminator, which corresponds to using the asymptotic values for the remaining coefficients [14] In practice, a cluster of atoms

is built around the atom  $i$  for which we wish to calculate the LDOS. The number of atoms in the cluster is determined by the requirement that all atoms should be reached from  $i$  within  $nc$  jumps. A great advantage of this technique is that we do not need to assume any periodicity of the system. In this work atom up to 10th nearest neighbors is considered, in term of cluster size this means that in each cluster around an atom 10425 atoms are considered.

### 3. LOCAL DENSITY OF STATES

The method is introduced to investigate transition metals and Pd is selected. In order to analyze electronic structures and modeling surfaces of transition metals the first stage is to calculate the local density of states of atoms at sites that are geometrically different from each others. At first the matrix representing hopping integral between first and second nearest neighbors in the bulk is calculated that result a  $8 \times 5 \times 5$  matrix when only  $d$  orbital in the wave function is considered. This matrix elements results from tight binding hopping integral and direction cosine between considered atom and its neighbors. In this work these tight binding parameters are used:

$$\begin{aligned} dd\sigma_1 &= -0.661470473 & dd\pi_1 &= 0.440980315 & dd\delta_1 &= -0.110245079 \\ dd\sigma_2 &= -0.116955645 & dd\pi_2 &= 0.07797043 & dd\delta_2 &= -0.01949260 \end{aligned}$$

As it is explained in model at the next stage the matrix elements of green operator in the atomic orbital basis set are calculated. This quantity in continued fraction is expanded and the coefficient of expansion by using recursion method is calculated. The question is how many moments should be included in the computation of the LDOS. In order to reach sufficient accuracy in the calculated energy 12 exact level in the continued fraction are used- ie 24 exact moments- for (111) surfaces. In term of cluster size it translates to at most 10425 atoms per cluster. It is assumed that potential perturbation occur on all atoms that can be reached in 12 first and 6 second nearest neighbor jumps from the central atom of the system (chosen to be an atom in the bulk). We calculate local density of states for an atom in the bulk and at the (111) surface of Pd:

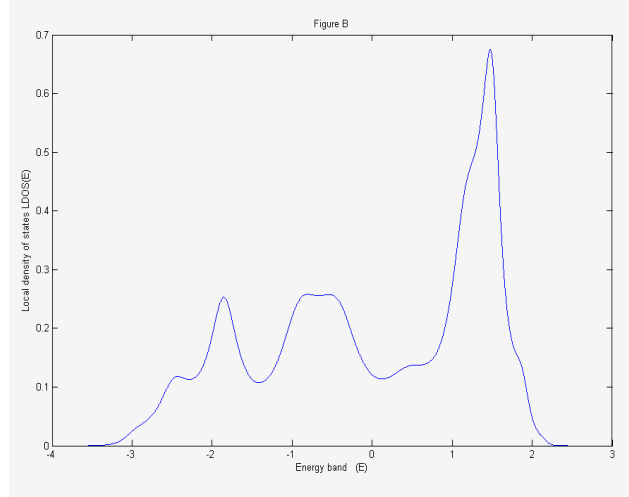


Figure 1: Local density of states for an atom at the (111) surface of Pd

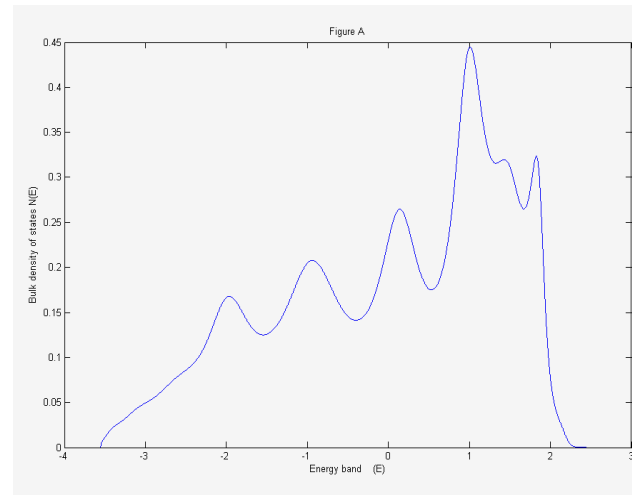


Figure 2: Local density of states for an atom in the bulk and at the (111) surface of Pd

When the LDOS of surface atom over energy band is integrated we saw that the total charge is not conserved and Fermi energy should alter such that total charge conserved.

### 4. SURFACE ENERGY

Surface energy in the form of a required energy is defined for separating an infinite crystal into two semi-infinite crystal in which intersect with special crystal orientation is confined. It is shown in the previous section that the total charge is not conserved in order to reconstructing the total number of electrons for the conservation proposes it is required to allow unreal (but small of Fermi level) to occur.

$$\delta E_{band} = 2LN \left[ \int_{-\infty}^{E_F + \delta E_F} En'(E)dE - \int_{-\infty}^{E_F} En(E)dE \right] \quad (9)$$

That  $n(E)$  and  $n'(E)$  is the LDOS of bulk and surface respectively. And  $L$  is the number of  $d$  orbitals. For small  $\delta E_F$  we have:

$$\delta E_{band} = 2LN \int_{-\infty}^{E_F} (E - E_F)n(E)dE \quad (10)$$

Electrons that is added or reduce is added or reduced to the Fermi level. By using the local density of states of surface and bulk atom that we presented in the previous section and above relation the surface energy is calculated and we result:  $\delta E_{band} = 0.0975 \text{ eV}$

If this value is compared with experimental value and other numerical value [8] there is a good agreement, however in this work there is an improvement because we also considered second neighbor interactions.

By using the technique presented in this paper the surface energy of other transition metals can be calculated in the series but it should attend that only for atoms at the end of transition metal series this relation can be used and for others must have some correction in relations.

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## 5. CONCLUSION

Surface energy of Pd is calculated in this method and it is shown that there is a good agreement with other works. In this work only  $d$  orbitals considered in model and it is concluded that for calculation the surface energy of Pd the role of  $d$  orbitals is majority. However considering only  $d$  orbitals is not the best model for calculation the energetic of all transition metals and  $s$  and  $p$  orbitals must be considered also. The technique that is introduced in this work does not need to assume any periodicity of the system and this is one of innovation of this method. The other innovation of this technique is that in this work atom up to 12th nearest neighbors is considered and the result is more accurate than other numerical result and has good agreement with experimental value.

In this work the reconstruction effect is avoided. Calculation of surface energy with reconstruction effect in tight binding model is also possible but it is an inconvenient numerical calculation.

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