The Importance of Surface Self-Energy in Metal/Metal-Oxide Adhesion

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Abstract

Starting with density functional theory (DFT) results, we correct the computed work of adhesion for Pd(111) to α-Al$_2$O$_3$(0001). Here polarization bonding dominates at the interface and is well described by DFT, but the surface energies of both the metal and the oxide must be altered for electron self-exchange and -correlation. This is accomplished using a jellium model as applied to surface electron densities obtained from the first principles calculations. We show that this correction is quite large for the generalized gradient approximation (GGA), thus explaining the difference between GGA results for metal/metal-oxide binding and those obtained by the local density approximation (LDA), where an accidental cancellation in errors produces better agreement with experiment. After the corrections, *both* methods produce results that are within the experimental error bars.

Durable interfaces between disparate materials, such as metals and metal-oxides [1], are critical for nanotechnology development. Strong binding is required for the manufacture of nanoscale microelectronics [2] and metal/metal-oxide interfaces are also of critical importance in technologies involving heterogeneous catalysis [3], sensors, and seals, and are central to basic issues dealing with corrosion and adhesion.

Despite the importance, the strength of the metal/metal-oxide interface is poorly known. Many published values, such as those determined from the take-off angle of metal droplets or from peel tests, disagree due to the presence of impurities or to mechanical contributions to the measurements, such as dislocation slip or the transfer of material across the boundary.

Especially in the last decade, studies done on well-defined samples in ultra high vacuum (UHV) have constructed a basis for qualitative and semi-quantitative comparisons. These studies have also eliminated some possible bonding mechanisms, such as the formation of covalent metal-oxygen bonds on the surfaces of highly ionic oxides. Several reviews have now been written [4].

Recently, the group of Besenbacher [5, 6] developed a method to determine quantitatively the work of adhesion (W_{adh}) between pure samples in UHV. Their method used scanning tunneling microscopy (STM) to measure the height of metal nanocrystals formed by deposition and heating. They then applied the classic theory of Winterbottom [7], which relates the heights of crystals in thermodynamic equilibrium with a substrate to the surface energies of the crystal and its adhesion, as reflected in the Wulff shape.

The substrate chosen was an ultrathin (~ 5 Å) two O-plane film of "γ-like" alumina grown on NiAl(110) by oxidation in UHV [8]. This film has been widely used in studies

of metal nanoparticles relevant to catalysis [3] and permits STM studies due to a lack of charging caused by the extreme thinness of the insulating structure. The W_{adh} values for Pd [5] and Cu [6] nanocrystals were both found to be 2.8 ± 0.2 J/m^2.

The interatomic spacing of Cu(111) compared with that of a basal plane of oxygen ions results in a 9% mismatch. Therefore, it is likely that this interface is incommensurate or that there are substantial unknown dislocations. To compute the incommensurate case would involve a unit cell of about 100 atoms per layer on Cu and 167 atoms per layer in the oxide. For this reason, we omit considering this system, but focus on the results involving Pd where the mismatch is a few percent and commensurability may be assumed.

Bogicevic and Jennison (BJ) [9] used first principles density functional theory (DFT) to determine the interfacial binding energies of a wide variety of metals on a model alumina film of the same thickness as that grown on NiAl(110). Because of domain rotations produced by a lattice mismatch, however, NiAl could not be used as a substrate. Instead, Al(111) was substituted as it has a good lattice match with a densely packed plane of O-ions. Because of previous work, it was assumed that all Al-ions occupied tetrahedral sites. The adhesion was determined by first separately finding the total energies of the relaxed metal (E_m) and oxide/Al (E_o) slabs, then the total energy of the relaxed slabs when together (E_{om}), or $W_{adh} = E_m + E_o - E_{om}$. BJ also analyzed the nature of Pd adhesion (0.7 eV/atom at 1 ML) and found that it was due to polarization (i.e., there is no significant covalency or charge transfer), as was proposed long ago [10]. BJ also found a rapid convergence of W_{adh} with metal film thickness. Finally, the BJ binding for 1 monolayer (ML) of Pt (0.6 eV/atom) is the same strength as that previously computed

using LDA and 1 ML Pt on the basal plane of sapphire, or α-Al_2O_3(0001) [11]. Here too polarization binding was found to dominate, the only difference being Pt occupies the atop Al sites while Pd takes the atop O-sites. This shows the similarity of the two surfaces for metal binding.

In the case of Pd, the BJ LDA value is in better agreement with the subsequently determined experimental number [5] than is GGA binding, which was *much* smaller. This is surprising because GGA is generally considered the superior method for energetics [12].

Subsequent work by Jennison and Bogicevic (JB) [13] used a more realistic film, a two O-layer film containing ¾ octahedral and ¼ tetrahedral site Al ions. This was found to be lower in energy than a film where all Al ions occupy the tetrahedral sites as used by BJ. (Mixed site occupancies are also believed to occur in the film on NiAl [8].) Now the unrealistic Al(111) substrate was found to dramatically change the binding because a redox reaction was observed. However, when a rigid Ru(0001) substrate was substituted, more like NiAl in this respect, the reaction did not occur and the LDA binding of Pd (0.8 eV/atom) was similar to BJ.

Thus, in the absence of a reaction, the calculations yielded about the same adhesion, with the JB value considered the most accurate model film for that used in the experiment [5]. This is due to the fact that the metal atoms sit atop the O-ions, and in all three cases the O-ions have high ionicity and the surface has 1/3 ML of Al-ions that are, in the absence of the metal, nearly coplanar with the O-ions.

The work of adhesion from the "realistic" alumina model slab described above [13] is 2.4 J/m^2 in LDA and 1.6 J/m^2 in GGA, compared with the experimental results of 2.8

J/m^2 by Hansen, *et al.* [5]. Note the GGA value is only 2/3 that of LDA and even LDA falls outside the error bars of the experiment, being about 17% low. Here we address the origin of the large LDA/GGA difference, the surprising observation that LDA seems nearly correct, and show that the explanation lies in the surface electron self-energies, which are neglected by both methods.

The slab energies may be separated into bulk and surface contributions, e.g. $E_m = E_m(bulk) + E_m(surface)$. Similarly, the combined slabs may be separated into the bulk and interfacial energies, $E_{om} = E_m(bulk) + E_o(bulk) + E_{om}(interface)$. By substitution, the above formula then becomes $W_{adh} = E_m(surface) + E_o(surface) - E_{om}(interface)$.

First, since the interfacial binding is due to polarization, $E_{om}(interface)$ is directly related to the electron density, $\rho(\mathbf{r})$. In Ref. [13], this was computed in LDA and in GGA. These numbers were available to us and we compared them in the interfacial region by taking slices from the Pd plane to the O plane.

We found that the largest relative density differences, i.e. $[\rho_{LDA}(\mathbf{r}) - \rho_{GGA}(\mathbf{r})]/\rho_{LDA}(\mathbf{r})$ are in the O-plane of the interface (Fig. 1). However, these amount to only a few percent. Since the polarization interaction should scale as the square of the image charges, $E_{om}(interface)$ is then the same for LDA and for GGA to well less than 10%. Thus to understand the large differences in the computed W_{adh}, we must look to the surface energies.

Here, our DFT [14] calculations used the Vienna *Ab initio* Simulations Package (VASP) [15] in the local density approximation (LDA) [16] and in the generalized gradient approximation (GGA) known as PW91 [17]. The ultrasoft pseudopotentials of Vanderbilt [18] describe this system to high accuracy with a plane wave cutoff of 270 eV.

Because of the long-range electrostatic forces in oxide as opposed to metallic systems, we used a large vacuum gap between the slabs, which repeat along the c-axis due to the plane wave basis set. We found ~ 15 Å or greater to be adequate.

Because these systems often display both hard and very soft vibrational modes, geometric relaxation must be done gently. We find a damped molecular dynamics algorithm with small timesteps almost always proceeds monotonically downhill in energy, leading to a fully relaxed geometry, where all residual forces are < 0.03 eV/Å.

Instead of using a model alumina film, where the geometry of the Al-sublattice is still not definitively determined, we used sapphire(0001) to model the oxide surface. As noted above, this surface [11] binds metal in the same manner and in quantitative agreement with the film studies [9, 13].

To obtain the sapphire surface electron density, we used a primitive unit cell in the x-y plane consisting of nine layers of O-ions, having three O-ions per layer. Both surfaces were fully relaxed in order to minimize the surface and eliminate the slab dipoles. The center three layers of O-ions, and their nearest Al-layers, were frozen at the bulk sapphire DFT positions. This was done separately using bulk LDA and GGA, which differ by less than 1% in lattice constant. Testing showed 6 k-points was converged to 0.02 eV in total energy. The resulting relaxations agree with those reported for a thicker slab [11]. This slab provides the near-surface charge densities and agrees with the thin film studies in that there is a close packed layer of O^{2-} ions with a nearly coplanar 1/3 ML of Al^{3+}.

The Pd slab consisted of seven layers with the middle three frozen at the LDA or GGA bulk positions. This provided the surface electron densities for the metal.

The general outline of our correction scheme for the surface self-energies is presented in Ref. [19] and consists of two steps. First a correction (energy/unit surface area) is determined from a reference system as a function of suitable, density related, parameters of this system. Then a mapping from the real system density to the reference system parameters is developed.

In Ref. [19] the correction is developed using an exponential model as a reference system. This correction is a function of the bulk density and a parameter describing the density profile at the surface.

Unfortunately this correction is, for the moment, only available for the exchange self-energy. So in this work we instead use the correction based on the jellium surface model developed in Ref. [20] which provides corrections for both exchange and correlation self-energies but only as a function of the bulk density (see Fig. 2).

In Ref. [19] the mapping from the "real system" (the same jellium surface model as we use as the reference system here) to the two parameter reference system (the exponential model) was done with a direct transfer of the bulk density and least squares fit for the profile. In Refs. [20] and [21], where a correction based on the jellium surface model is used (Fig. 2), the one-parameter mapping is done via the mean bulk density of the real system (Al, Pd, Pt, and Mo vacancies). This is appropriate for a vacancy system that is mainly bulk (in addition the error obtained by this crude mapping is over-shadowed by the crude estimate of the surface area of the vacancy). In this paper we will refine this mapping in order to improve the accuracy of this scheme so that it can be used on general flat surfaces (curved surfaces will be addressed in a forthcoming paper).

Let us start by estimating a *lowest* bound on the correction by also in this case using

the mean bulk density. That this gives a lower bound can be illustrated thusly: An uncharged system where the ions are smeared into a positive background charge density (a jellium system) will have a constant negative (electron) charge density, the mean density. When the positive background charge is gathered into real ions more electrons will gather around the ions and the space between ions will have a lower density than the mean density. We will then have higher density in ion planes than in planes not containing ions. The surface can be seen as such an ion plane where the density is higher than the mean density. The mean bulk density (from our calculations) is 0.64 Å^{-3} for Pd and approximately 0.56 Å^{-3} for sapphire. This gives a LDA (GGA) correction of 0.19 (0.46) J/m^2 for the Pd(111) surface and 0.16 (0.40) J/m^2 for the sapphire surface. The lowest bound for the work of adhesion is then 2.7 (2.5) J/m^2.

As seen in Fig. 3, where the mean density in cuts orthogonal to the z-axis is shown for both Pd(111) and sapphire surfaces, the surface indeed has a higher mean density than the overall mean bulk density. A better estimate can be done using this surface mean density. We estimate the mean surface density to be 0.975 Å^{-3} for Pd and 1.105 Å^{-3} for sapphire. This gives a LDA (GGA) correction of 0.28 (0.66) J/m^2 for the Pd(111) surface and 0.32 (0.74) J/m^2 for the sapphire surface. The work of adhesion estimated in this way is 3.0 J/m^2 in both LDA and GGA.

Taking the mean density in cuts orthogonal to the z-axis in the slabs is equivalent to average the density over the surface of spheres around the center of a vacancy.

The validity of using the mean density as input in the correction formulas is based on two assumptions: That the correction to first order scales linearly with bulk density (as seen in Fig. 2) and that the surface is flat (or perfectly spherical in the vacancy case).

Based on the nearsightedness principle [22], we can obtain a more fundamental estimate by determining the bulk density from every density profile orthogonal to the surface. To treat curved surfaces, the position of the surface in the profile should be determined; we leave that for a future publication and here concentrate on determining the bulk density. We will argue, though, that the surfaces in the Pd/α-alumina case are fairly flat and that taking the curvature into account (through adjustment of the size of the surface elements) would make a very small difference.

Let us start this part of the discussion by estimating an *upper* limit for the work of adhesion. First, assume the surface is flat and our points are evenly distributed in the x-y plane so that all our surface elements are of equal weight. Then assume in every cut that the first maximum of the density is the bulk density. Then, by determining the corresponding correction and adding them weighted by the appropriate surface element area, we obtain LDA (GGA) corrections of 0.32 (0.73) J/m^2 for the Pd(111) surface and 0.31 (0.71) J/m^2 for the sapphire surface. An upper bound of the work of adhesion is then 3.0 J/m^2 for both LDA and GGA.

By these considerations we have established the calculated work of adhesion for the Pd/sapphire(0001) interface to be between 2.7 and 3.0 (2.5 and 3.0) J/m^2 in LDA (GGA), a range close to the experimental accuracy and agreeing with the experimental number. Note also that LDA and GGA now give practically the same number, a highly desirable situation for computational work.

For the main purpose of this paper the above considerations are sufficient, but the ultimate goal is to be able to treat general surfaces automatically in a computer code. In addition, we want to have *better* accuracy than experiment.

While using the first maximum in a density profile as the bulk density will always give an upper limit and the mean overall density a lower limit, let us now elaborate on where the *position* of the surface should be taken to be. A point common for all surfaces is the point where the Laplacian (∇^2) of the density is zero. When approaching a surface from vacuum, the rate at which the density rises first increases, then but at $\nabla^2\rho(\mathbf{r}) = 0$, the rate starts to diminish, eventually making the density turn downwards again after the first ion plane. (At surfaces like Pd(111), where the ion planes are well separated, this will always be the case. But with more complicated systems, like sapphire, profiles occur with saddle points where the density does not diminish between ion planes, but continues upward into the density around an ion in the second plane. However, the number of points where profiles have saddle points is a small fraction of all points, so mistreating these points will give a negligible error.)

From examining the flat jellium surface model it is easily seen that the positive background is situated outside (towards the vacuum) of the point at which the Laplacian is zero. With the bulk density in the range 0.1 to 6.5 Å^{-3}, appropriate for surfaces we are examining here, the positive background is situated only a fraction of an angstrom outside of this point. A good measure of the flatness of the surface is thus obtained by mapping out the surface where $\nabla^2\rho(\mathbf{r}) = 0$. In the case of Pd(111), the buckling is very small, only 0.34 Å (compare with the distance between Pd(111) planes, 2.3 Å). In the sapphire system the buckling is larger due to Al-ions near the O-plane at the surface. The buckling is 1.1 Å compared to an O-plane distance of about 2.1 Å. Since the density is low at the Al-ions and the correction therefore small, neglecting the fact that the surface elements are larger here only produces a small error in the total correction.

Since the place where $\nabla^2\rho(z) = 0$ is an unambiguous point that always exists on a line intersecting the surface, it is convenient to use this point when determining the bulk density for each density profile. We here give a procedure that works well in this case and has potential to work well also in other cases.

With the help of the density at the point in a profile $\nabla^2\rho(z) = 0$, we pick the jellium surface that has this same density in its $\nabla^2\rho(z) = 0$ point. In Fig. 4, such a Pd(111) profile is shown together with the corresponding jellium surface.

We note that the bulk density of the jellium surface profile is higher than the first real maximum density, but that the profiles agree amazingly well near the surface. We believe that the poorer agreement inside the metal is due to our use of pseudopotentials. In a pseudopotential calculation, the core electrons are replaced by a modified potential that has the same influence on the valance electrons that the core electrons should have. The core electron density is not calculated, though, which leaves the interior of a material with less electron density than the electrons at the surface believe. This viewpoint is also corroborated in Fig. 5 where a profile is shown through a Pd-ion in the surface. As expected, the agreement of the Pd(111) and the jellium profile is not at all as good due to the missing core electron density.

Note that the correction should be calculated with the same density as is used when calculating the exchange-correlation energy in the first place. If the core electrons are not in this calculation, they should not be added when calculating the correction.

In Fig. 4 and 5, a line representing 75 % of the bulk jellium density is shown as well. Even though the overall profiles do not agree, the 75 % figure always seems to agree reasonably well with the expected bulk density of a Pd(111) profile.

Using as the bulk density in the correction scheme, this value of 75 % of the bulk density obtained from a jellium surface whose density at $\nabla^2\rho(z) = 0$ is the same as the real profile, gives corrections of 0.27 (0.62) J/m^2 in LDA (GGA) for the Pd(111) surface and 0.28 (0.63)) J/m^2 in LDA (GGA) for the sapphire surface. Thus we observe that this scheme produces the best overall corrections, yielding works of adhesion for the Pd/α-alumina interface of 2.9 J/m^2, obtained from *both* LDA and GGA.

These results are very encouraging and illustrate both a method to correct the computed surface energies of solids and also to correct the related adhesion values. However, these interfaces are relatively weak. Although the binding is much stronger than van der Waals forces, it is much weaker than covalent bonds or those produced by charge transfer between the materials. Thus in general, interfaces exist where the adhesion is intermediate between LDA and GGA values or, in the case of substantial covalency, is even better given by GGA. In the present case, the weak bonding has made the surface self-energies fractionally a larger part of the adhesion energy, even though these energies are, of course, always present. In conclusion, we have used experimental data to show that jellium results can be used to correct the surface energies to good accuracy, and that the magnitude of the corrections are about the same for metal and for oxide surfaces.

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References

1. *The Surface Science of Metal Oxides*, Faraday Discussion **114** (2000).

2. For example, M. F. Gillies, A. E. T. Kuiper, and G. W. R. Leibbrandt, J. Appl. Phys. **89** (2001) 6922; S. Tehrani, B. Engel, J. M. Slaughter, E. Chen, M. DeHerrera, M. Durlam, P. Naji, R. Whig, J. Janesky, J. Calder, IEEE Trans. on Magnetics **36** (2000) 2752; E. Y. Chen, R. Whig, J. M. Slaughter, D. Cronk, J. Goggin, G. Steiner, S. Tehrani, J. Appl. Phys. **87** (2000) 6061.

3. G. Ertl and H.-J. Freund, Physics Today **52** (1999) 32, and references therein.

4. C. T. Campbell, Surf. Sci. Rep. **27** (1997) 1; C. R. Henry, Surf. Sci. Rep. **31** (1998) 231; M. Bäumer and H.-J. Freund, Prog. Surf. Sci. **61** (1999) 127.

5. K. H. Hansen, *et al.*, Phys. Rev. Letts. **83** (1999) 4120.

6. T. Worren, *et al.*, Surf. Sci. **477** (2001) 8.

7. W. L. Winterbottom, Acta. Metall. **15** (1967) 303.

8. R. M. Jaeger, H. Kuhlenbeck, H.-J. Freund, M. Wuttig, W. Hoffmann, R. Franchy, and H. Ibach, Surf. Sci. **259** (1991) 235.

9. A. Bogicevic and D. R. Jennison, Phys. Rev. Letts. **82** (1999) 4050.

10. A. M. Stoneham, Appl. Surf. Sci. **14** (1983) 249; M. W. Finnis, A. M. Stoneham, and P. W. Tasker, in *Metal Ceramic Interfaces*, M. Rühle, A. G. Evans, M. F. Ashby, and J. P. Hirth, eds. (Oxford: Pergamon, New York, 1990), p. 35.

11. C. Verdozzi, D. R. Jennison, P. A. Schultz, and M. P. Sears, Phys. Rev. Letts. **82** (1999) 799.

12. L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94** (1991) 7221.

13. D. R. Jennison and A. Bogicevic, Surf. Sci. **464** (2000) 108.

14. P. Hohenberg and W. Kohn, Phys. Rev. **136** (1964) B864; W. Kohn and L. J. Sham, Phys. Rev. **140** (1965) A1133.

15. G. Kresse and J. Hafner, Phys. Rev. B **47** (1993) 558; **49** (1994) 14251; **54** (1996) 11169.

16. J. Perdew and A. Zunger, Phys. Rev. B **23** (1981) 5048; D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45** (1980) 566.

17. J. P. Perdew et al., Phys. Rev. B **46** (1992) 6671.

18. D. Vanderbilt, Phys. Rev. B **32** (1985) 8412; **41** (1990) 7892.

19. A. E. Mattsson and W. Kohn, JCP **115** (2001) 3441.

20. T. R. Mattsson and A. E. Mattsson, preprint.

21. K. Carling, G. Wahnstrom, T. R. Mattsson, A. E. Mattsson, N. Sandberg and G. Grimvall, Phys. Rev. Letts. **85** (2000) 3862.

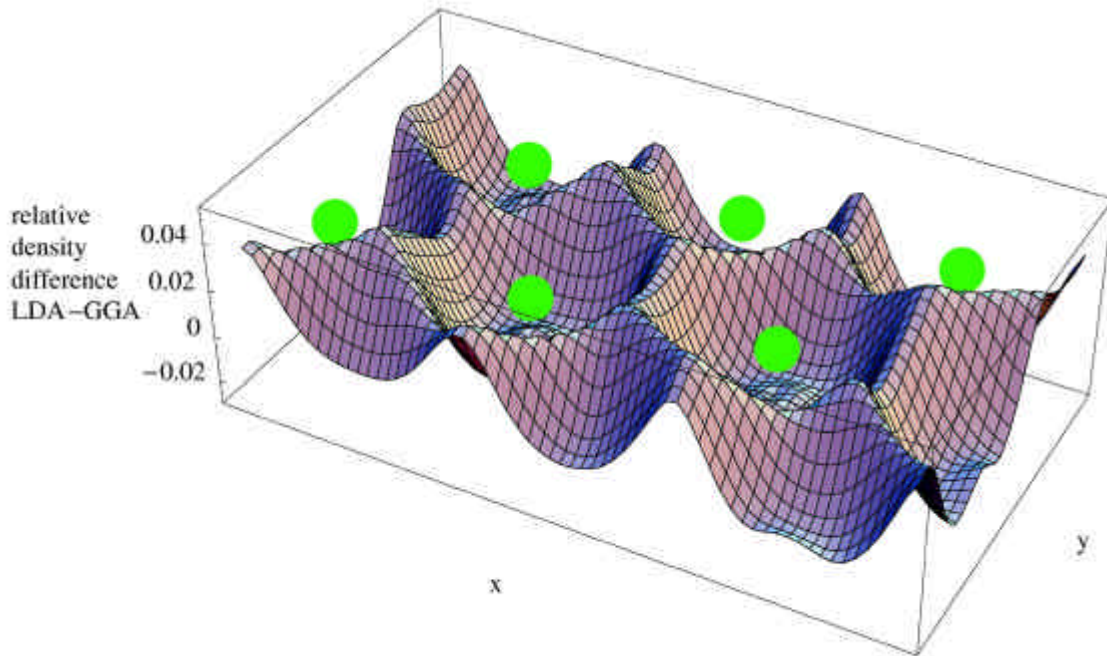22. W. Kohn, Phys. Rev. Lett. **76** (1996) 3168.

Fig. 1: Relative electron density through the O-plane at the Pd/alumina interface. Other slices show lesser differences. The green dots indicate the positions of the O-ions in the x-y plane.
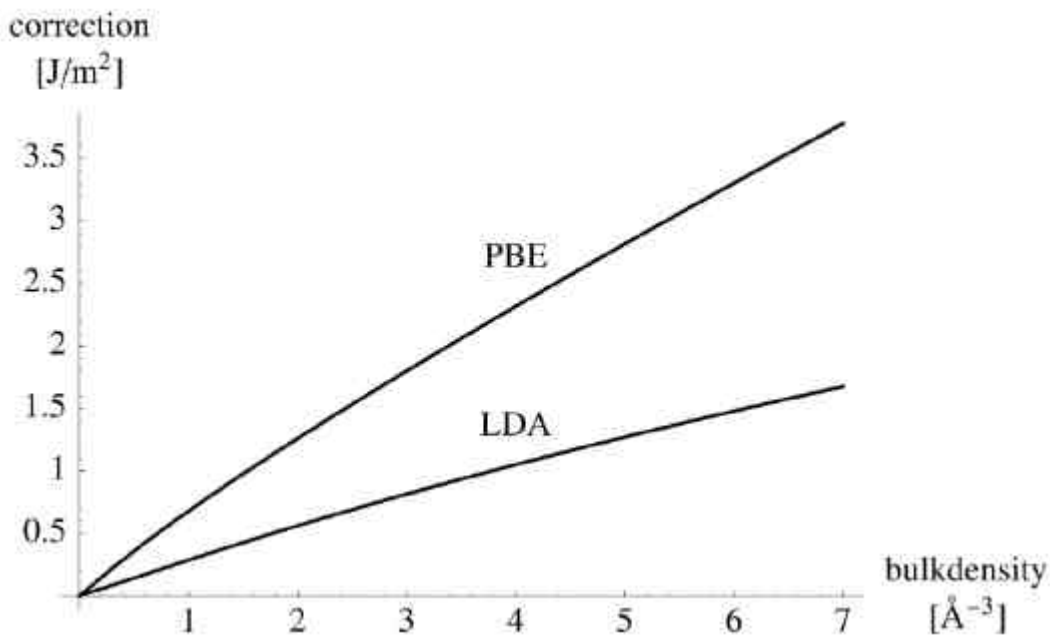

Fig. 2: Corrections for the surface intrinsic error in LDA (GGA) calculations. The difference between the PBE type of GGA and the PW91 type used in the calculations in this paper is negligible. This correction is extracted from jellium surface systems [20] and is given as a function of the bulk change density.
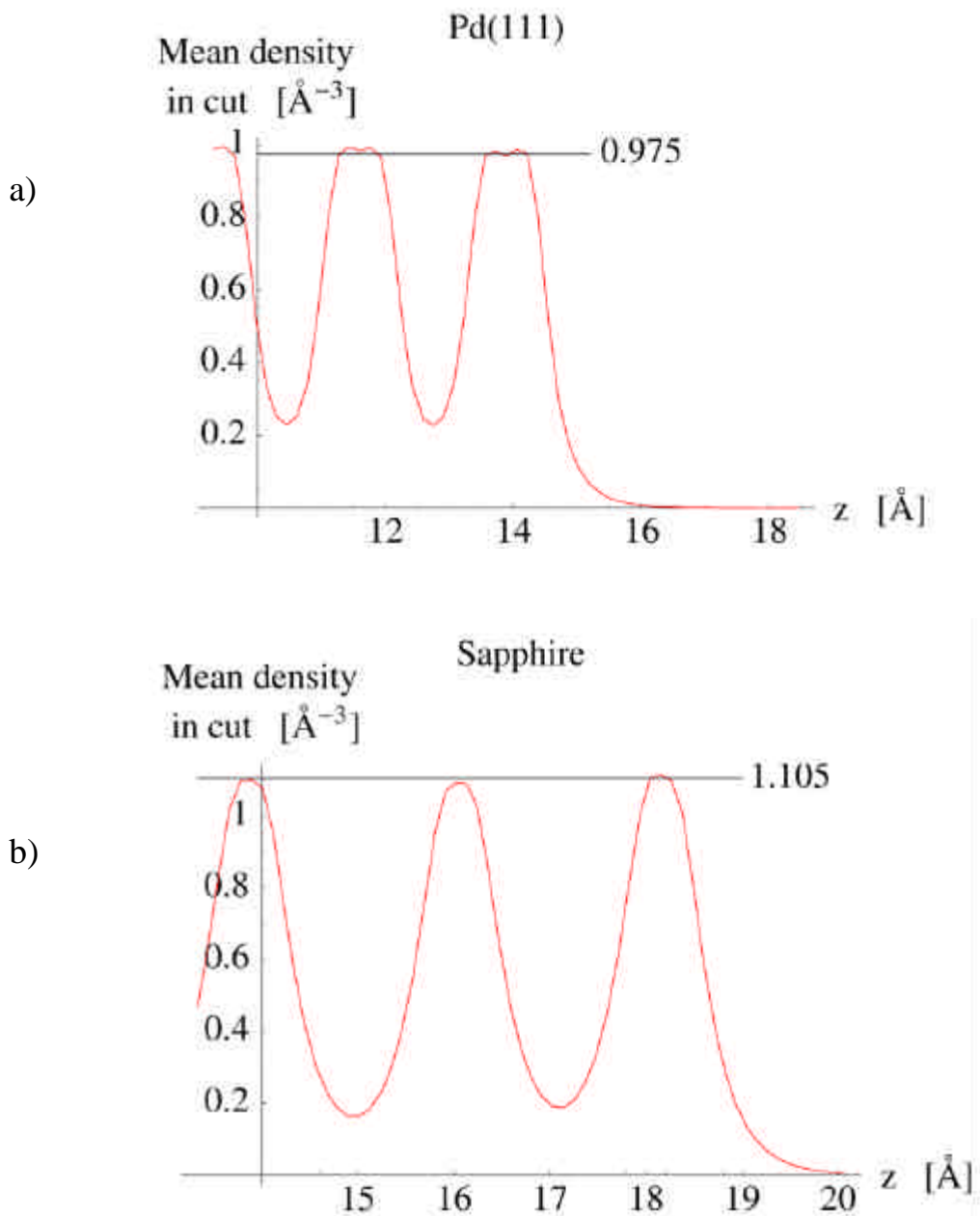
Fig. 3: The mean density in cuts orthogonal to the z-axis for a a) Pd(111) b) sapphire surface. The surface mean density is higher than the mean overall density (0.64 and 0.56 A^{-3} for the Pd(111) and sapphire surfaces respectively). Shown are also the estimated mean surface densities, 0.975 and 1.105 A^{-3} respectively.

Charge density profile perpendicular to the surface midway between two neighboring surface atoms at a Pd(111) surface
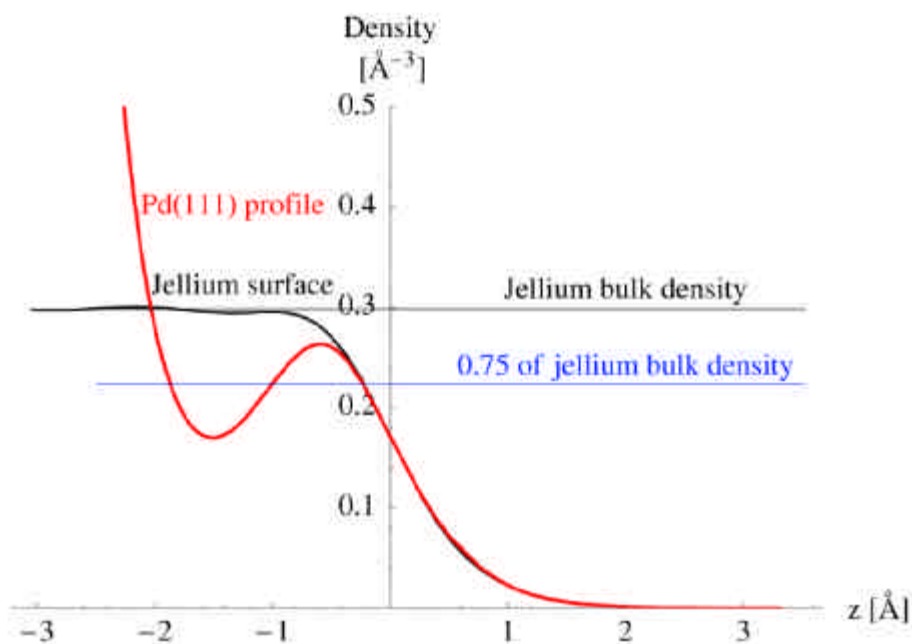
Fig. 4: Charge density profile midway between two neighboring surface Pd-ions at a Pd(111) surface. This profile coincides with the corresponding jellium surface profile near the surface. Due to the pseudopotential used to model the Pd-ion core electrons the agreement is poorer inside of the surface. 0.75 of the jellium bulk density agrees reasonable well with the expected bulk density of the Pd(111) profile.
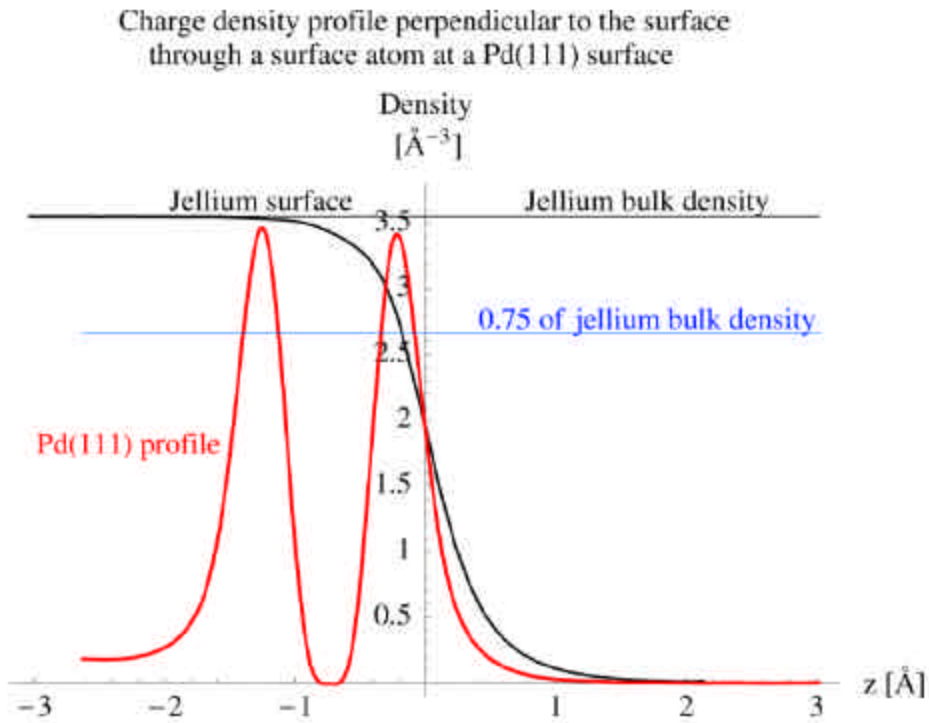
Charge density profile perpendicular to the surface through a surface atom at a Pd(111) surface

Fig. 5: A change density profile through a Pd-ion on a Pd(111) surface. Due to the pseudopotential this profile do not agree well with the corresponding jellium surface profile. However, as in Fig. 4, 0.75 of the jellium bulk density agree reasonably well with the bulk density of the Pd(111) profile.