Quantum size effects of Pb overlayers at high coverages

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We have studied Pb thin films as a function of the thickness up to 60 monolayers (MLs) using *ab initio* first principles and model calculations. Magic heights corresponding to a modulated oscillatory pattern of the energy of Pb(111) films have been measured up to about 30 MLs. We demonstrate that this behaviour continues even for higher thickness due to an extra second modulation pattern in the energetics of the metal film as a function of the number of atomic layers. The origin of this second modulation is the nesting of two close values of the Fermi wavelength in the (111) direction.

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1. Introduction

Quantum size effects (QSEs) are a key issue to understand the physical properties of nanostructures. They show up in the stability of clusters or nanowires, which is favored for some values of their radius, so-called "magic"[1,2]. This behaviour has been shown to affect also the growth of islands or thin films over surfaces. In particular, these effects are very strong for Pb(111) films, which can form wide flat films of preferred thickness. Monitoring the growth of Pb nanoislands over Cu(111) [3] or Si(111) [4] with different experimental techniques (such as He atom scattering (HAS) [5], Scanning Tunnelling Microscopy (STM)[3], photoemission and Surface X-ray diffraction) has revealed the preference of Pb for bi-layer growth [6].
The origin of the "magic" height selection is easy to understand qualitatively with a simple picture of electrons confined in a potential well [7]: valence electrons fill paraboloidal subbands and, as the thickness of the slab is increased new quantum well states are occupied, producing oscillations in the energy and related physical properties with periodicity $\lambda_F/2$ (λ_F is the Fermi wavelength of electrons in Pb). When the interlayer spacing (d) of Pb in the (111) direction is considered, the approximate relation $d \approx 3\lambda_F/4$ gives rise to a beat pattern superimposed to the oscillations [8,6] with an even-odd change in the magic number of atomic layers at the beats. The energy minima can be related to the magic or more stable thicknesses measured in the experiments. A quantitative description of the measured magic sizes, on the other hand, requires more sophisticated models. In some studies the support has been included to provide an accurate description of the experiments [8–10]. There are several theoretical works devoted to the study of QSEs in

thin films within the density functional theory (DFT). In this paper, we explore larger sizes (up to 60 MLs) of Pb thin films than considered in the literature by using *ab initio* calculations, which include the atomic structure of Pb films. We find a second extra modulation of the oscillations in the energetics of the thin films and explore the origin of this new modulation and its effect on the stability at higher coverages than measured up to now.

2. Ab initio first principles calculations

We have analized the stability of free-standing Pb(111) films as a function of the number of monolayers (N), up to N=60 ML, taking into account the atomic structure. As the stability is given by the energy of the slabs, we have calculated first the total energy as a function of N. In this study we are not interested in the quantitative agreement with the experiments, but on the amplitude and the general trend of the oscillations for thicker films than studied up to now (N >30). Previous jellium calculations [8] studied the effect of the support, but in that approach only one value of the Fermi wavevector is involved, *i.e.*, a spherical Fermi surface is assumed. The support can introduce a shift of these oscillations but this is not the topic of our work. The key of *ab initio* calculations is that they provide a more realistic description of the Fermi surface.
Our calculations have been performed with the VASP code [11] by using the generalized gradient approximation (GGA) [12] for the exchange-correlation potential and the projector augmented-wave method (PAW) [13]. Convergence of the energies versus plane-wave cutoff (237 eV), k-mesh (22x22), and vacuum (10 ML) have been chosen to get high accuracy. These values are in agreement with ref. [14]. Previous *ab initio* calculations for a small number of layers included the lattice relaxation [15], but we have considered bulk distances between atoms. This relaxation would affect only the position of the first beat, and it is not so important for the present study.
To analyse the stability we have calculated the second derivative of the energy versus the number of monolayers. The results are shown in Fig. 1 with continuous line. Notice the minus sign, so that the minima correspond to stable films, as in previous jellium calculations. With the aim of comparing with the $1/D^2$ damping of the oscillations reported by jellium calculations [16], we have multiplied the second derivative of the energy times the square of the slab thickness. First of all we observe modulated oscillations, like "packets", with a period of about 8 ML. Between these "packets" there are beats with an even-odd slip in the magic thickness. This trend is similar to the jellium results reported in the literature. For N <10 ML there are slight differences, the first beat is moved upwards. The interface properties with the substrate and the relaxation effects also can affect at these coverages, but we are not interested in that region [8,9]. For larger coverages we observe a stronger damping in the *ab initio* result than the inverse square law observed for jellium. In addition, the distance between beats changes. This is more evident for N >30 ML, and around 40 ML the period decreases to about 6.4 ML.

3. Comparison with analytical models

Jellium model calculations assume one value of the Fermi wavelength, close to 7.5 a_0 for Pb(111). Within that model, the energy oscillations times the square effective thickness

(D_{eff}) of the film can be fitted to a simple sinusoidal expression which reproduces the beat pattern:

$$\sigma_{osc} D_{eff}^2 = \sin[2k_F(dN + \delta_0)] \quad (1)$$

where δ_0 is a surface shift that accounts for the charge spill-out at the surfaces, d is the interlayer spacing, and N is the number of layers.
Our *ab initio* results could not be fitted with expression (1), i.e, using one value of k_F in the whole thickness range, but we succeeded to fit nicely the *ab initio* values with a superposition of two sinusoidal expressions for two very close values of k_F. We tried the following analytical description of Fig. 1:

$$A_1 \sin[2k_{F1}(dN + \delta_0)] + A_1 \sin[2k_{F2}(dN + \delta_0)] \quad (2)$$

where k_{F1} and k_{F2} are two close Fermi wavevectors in the (111) direction and A_1 and A_2 are their corresponding weights. The fit to such expression using λ_{F1}=7.47a_0, λ_{F1}=7.54a_0, A_1=0.72 and A_2=1.28 is really good. The result is an extra modulation over the first modulation, which gives the "packets" and first beats described by one value of k_F. This second modulation produces an extra second quantum beat, responsible for the stability at coverages over 30 MLs. The values of k_F used for the fitting to the analytical expression (2) are very close to the values reported in the literature. The second Fermi wavelength arises because the section of the Fermi surface for Pb is not circular but has a butterfly shape [17,3], as shown in the inset of Fig. 2. In a different context, the deviation of the Fermi surface from the spherical shape has been found to affect the magnetic interlayer coupling in multilayers, being important for distances as long as 100 MLs [18]. The values of the nesting wavelengths underlying the oscillations obtained with *ab initio* calculations are extracted from their Fourier transform, plotted in Fig. 2 with continuous line. In the same plot we show the peaks corresponding to the analytical expressions that assume one (dotted line) and two (dashed line) Fermi wavevectors given by Eqs. (1) and (2), respectively. We notice that both beat frequencies for the analytical model of Eq. (2) have merged into a broad peak in the *ab initio* calculations. In part, this is due to the actual window of layer sizes.
In the inset of Fig. 2, the behaviour of the oscillations with one k_F (circular section of Fermi surface) is shown as compared to the two k_F nesting behaviour, corresponding to the butterfly like section of the Fermi surface. The one k_F case produces a modulated oscillating structure, but the two k_F plot gives a more rich pattern with a second modulation. In that sketch, two k_F values with the same weight have been considered, so that the second quantum beat is clearly distinguished, and it is not accompanied by a slip from even to odd at that beat. This sketch explains already the origin and the trend of the *ab initio* results displayed in Fig. 1, but is not exactly the same, due to the different weights of the wavevectors.

4. Conclusions

We have shown that there are new features (a second modulation structure) in the quantum oscillations of Pb thin films at high coverages (N >30 ML), about the borderline of the thickness explored by experiments up to now. We have obtained a good

description of the energy oscillations obtained with *ab initio* calculations (N <60 ML) using sinusoidal expressions with two similar nesting Fermi wavelengths. The agreement is not good in the whole thickness range studied when only one value of the Fermi wavelength is considered. The second modulation of the energy oscillations would account for the magic stability of thin films at high coverages. Anyway, more experiments would be helpful at higher coverages (N >30 ML) in order to check this effect.

5. Acknowledgements

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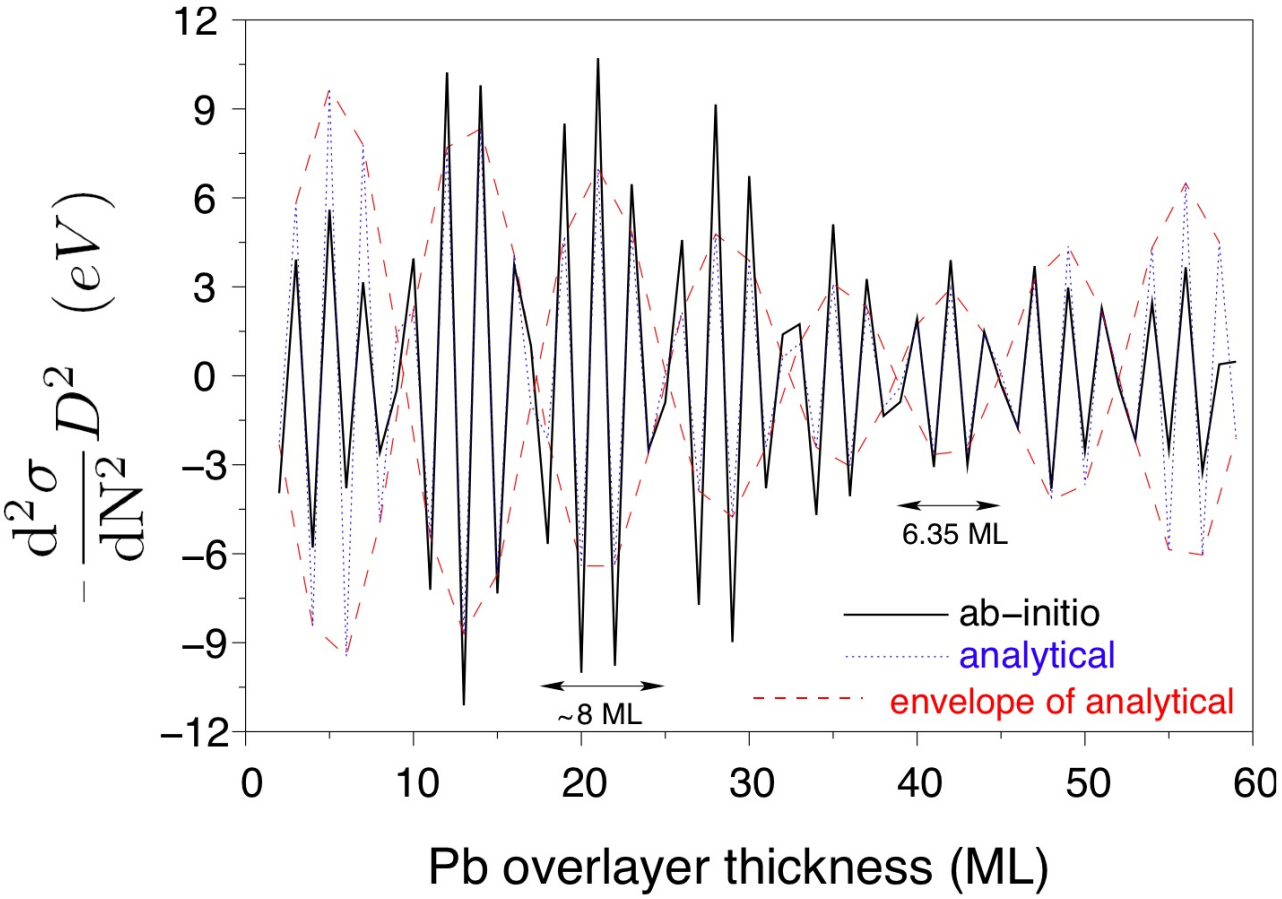

Figure 1. Second derivative (minus sign) of the energy per surface atom times the square of the Pb slab thickness versus the number of ML's (continuous line). The dotted line is the analytical curve obtained with two values of the Fermi wavelength (see the text) as given by equation 2. The dashed line is the envelope function of the analytical curve.

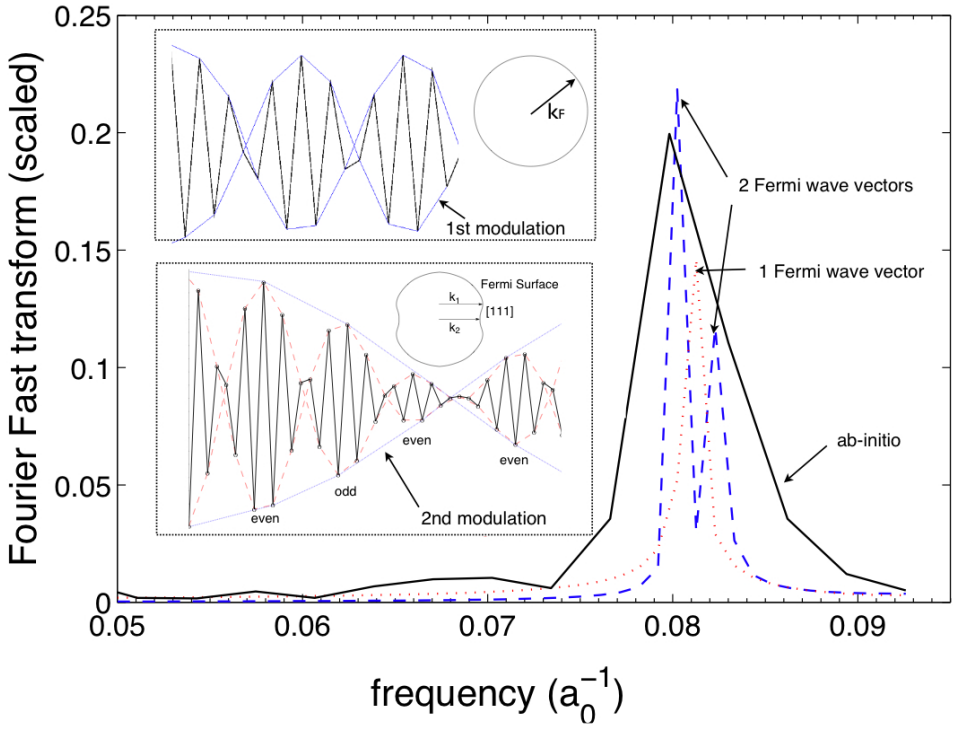

Figure 2. Fourier transforms of energy oscillations. First-principle calculations are given with full line; analytical expressions for one and two wavelengths [equations (1) and (2)] are shown with dot and dashed lines respectively. In the plot, the window of the analytical transforms is three times the one of *ab initio* calculations. In the inset the oscillations corresponding to one and two Fermi wavevectors are sketched.