

Quantum size effects in Pb layers with adsorbed Kondo adatoms: Determination of the exchange coupling constant

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We consider the magnetic interaction of manganese phthalocyanine (MnPc) adsorbed on Pb layers that were grown on a Si substrate. We perform an *ab initio* calculation of the density of states and Kondo temperature as a function of the number of Pb monolayers. Comparison to experimental data [Y.-S. Fu *et al.*, Phys. Rev. Lett. **99**, 256601 (2007)] then allows us to determine the exchange coupling constant J between the spins of the adsorbed molecules and those of the Pb host. This approach gives rise to a general and reliable method for obtaining J by combining experimental and numerical results.

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Strong correlation phenomena built the fundamental of a number of extraordinary effects observed in condensed-matter systems. One of the most drastic manifestations is the Kondo effect,¹ arising from strong coupling between single localized spins and the conduction electrons. For an antiferromagnetic-type interaction below the characteristic Kondo temperature, T_K , this coupling cannot be treated perturbatively. It comes along with the formation of a narrow peak in the density of states (DOS) of a Kondo adatom pinned to the Fermi energy of the conduction electrons, ε_F . Its line shape can be described by the well-known Doniach-Sunjic formula.^{2,3}

The appearance of the Kondo resonance has various physical consequences. In the context of the transport properties of bulk diluted magnetic alloys it manifests as the enhancement of the resistance at low temperatures. In mesoscopic systems consisting of a single quantum dot coupled to a pair of one-dimensional leads^{4,5} it results in a drastic enhancement of the conductance below T_K .^{6,7}

A system that recently has attracted much attention, both from the experimental and theoretical sides, is composed of a metallic host surface with a Kondo adatom (adsorbed atom) and a scanning tunneling microscopy tip, nonferromagnetic or ferromagnetic.⁸ Contrasting the case of a single quantum dot coupled to leads, such a system demonstrates a much greater variety of transport regimes. This arises from the possibility of quantum interference between distinct transport paths, namely, direct tip-host tunneling and indirect tip-adatom-host tunneling.⁹ In particular, the latter process gets extremely efficient for temperatures below T_K due to the appearance of a Kondo resonance in the adatom spectral function. The quantum interference mechanism leads to an asymmetry of the Kondo resonance. Instead of a Lorentzian line shape it acquires a Fano-type line shape, which is a characteristic of interference between a discrete level and a continuous spectrum. The appearance of this kind of a Fano-Kondo resonance has been found in various experiments with nonmagnetic tips⁹⁻¹² and has been discussed in a number of theoretical works.¹³⁻¹⁵

In a recent experimental work the quantum size effect on the Kondo temperature was investigated by Fu *et al.*¹⁶ The

system under study consisted of individual manganese phthalocyanine (MnPc) molecules adsorbed on ultrathin Pb films grown on Si(111). Scanning tunneling spectroscopy shows asymmetric Fano-Kondo peaks in the differential conductance. One central implication of the work by Fu *et al.*¹⁶ is that the variation in the film thickness, given by the number of Pb monolayers (MLs), leads to drastic changes in T_K , more specifically to pronounced oscillations with a period of 2 ML. The lowest (23 K) and highest (419 K) values occurred at thicknesses of 15 and 17 ML, respectively. Because the Kondo temperature scales with the electronic DOS at the Fermi energy, $\rho = \text{DOS}(\varepsilon_F)$, according to

$$T_K = A e^{-1/(J\rho)}, \quad (1)$$

where A is an amplitude and J is the exchange coupling constant, this observation has been attributed to oscillations in the Pb DOS with the film thickness. Indeed, for every 2 ML increase in the thickness one empty quantization band moves down below the Fermi level and gets occupied.¹⁷

In the following we present a state-of-the-art *ab initio* investigation of the electronic structure of Pb films on a Si(111) surface. Determining $\rho = \text{DOS}(\varepsilon_F)$ as a function of the film thickness and using Eq. (1) we can perform a fit to the experimental data given in Fig. 2 of Ref. 16. Besides the amplitude A , the exchange coupling constant J is the only fitting parameter and therefore can be obtained without any further assumption.

Our analysis is based on the augmented spherical wave approach, applying density-functional theory within the local density approximation.¹⁸ This method is particularly suitable for dealing with unit cells containing many atoms,¹⁹⁻²¹ which are needed to describe interfaces, since it utilizes a minimal atomiclike basis set. For the present system this basis set consists of Si $3s$, $3p$, $3d$, as well as Pb $6s$, $6p$, $5d$ states, and is complemented by orbitals of additional augmentation spheres. Brillouin zone integrations are performed using the linear tetrahedron method, where we checked the convergence of the calculation with respect to the fineness of the k mesh by means of a growing number of up to 231 k points in the irreducible wedge of the supercell Brillouin zone.

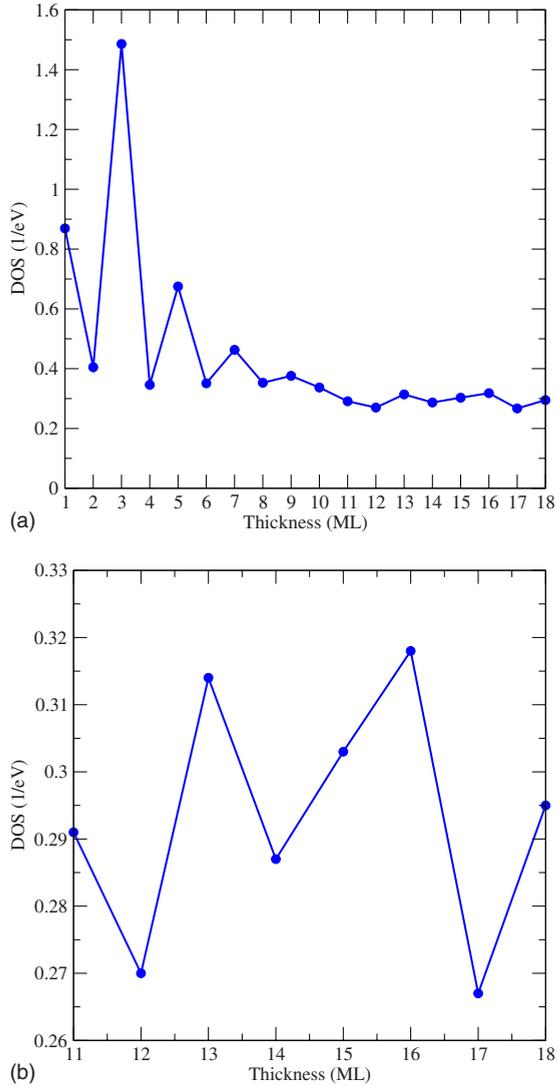


FIG. 1. (Color online) Top: total DOS at ε_F for a Pb(111) film on Si(111), depicted as a function of the number of Pb MLs. The values are normalized by the numbers of Pb atoms in the supercells. Bottom: zoom in for the 11–18 ML range.

Our Si(111)/Pb(111) supercells comprise of a Si slab of about 25 Å thickness, an attached Pb slab ranging from 1 to 18 Pb MLs, and a vacuum slab on top. For generating the supercells we have started from the hexagonal representation of the fcc lattice, with the (111) direction along the hexagonal c_{hex} axis. For the Pb slab we use the experimental lattice constant $a_{\text{Pb}}=4.95$ Å. Moreover, for attaching the Si slab ($a_{\text{Si}}=5.43$ Å) to the Pb slab we have to artificially shrink the former and introduce a lattice strain. Although this lattice strain in the Si slab is substantial, no drawback on the Pb electronic structure is to be expected since there are no Si states in the vicinity of the Fermi energy. Our supercells extend 121.25 Å along c_{hex} and have as basal plane a parallelogram with a 60° interior angle and edges of length a_{Pb} .

We obtain for the DOS at the Fermi energy the results displayed in Fig. 1 as a function of the Pb film thickness. One clearly identifies the previously discussed oscillatory behavior, with a period of 2 ML up to a thickness of 9 ML.

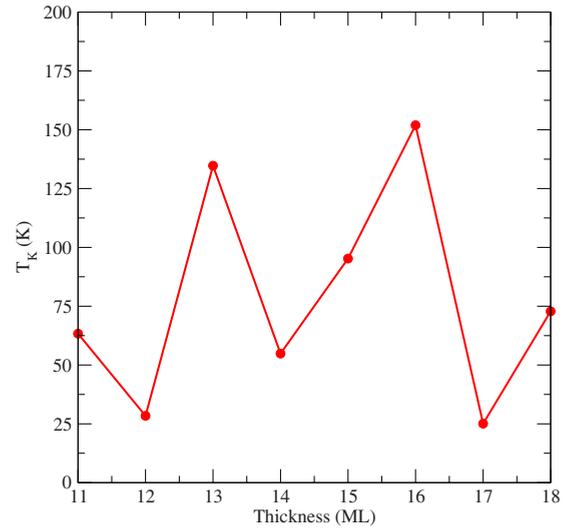


FIG. 2. (Color online) Kondo temperature as a function of the thickness of the Pb(111) film, given by the number of Pb MLs.

Deviations from this regular scheme are found in the intervals of 9–12 and 14–16 ML, where the oscillations are suppressed.²² Comparing Fig. 1 to the experimental data¹⁶ indicates that our curve is shifted by 1 ML to the left-hand side, see particularly the position of the 14–16 ML anomaly. This difference might either trace back to the experimental difficulty in counting the MLs or to the effects of the (planar) MnPc molecule on the local DOS, which is not included in our treatment. Since there is no ambiguity in the choice of the matching conditions at the Si-Pb interface, our approach elsewhere should not lead to a 1 ML shift.

Using Eq. (1) we next calculate from our DOS data the dependence of the Kondo temperature on the film thickness. To that aim, we use the second highest (150 K at 12 ML) and smallest (23 K at 15 ML) of the experimentally observed T_K values to fit the free parameters A and J . The correctness of the highest measured temperature (419 K at 15 ML) is quite dubious (see the discussion of the authors themselves) and thus not taken into consideration. At the Fermi energy, the *ab initio* DOSs amount to 0.318 eV⁻¹ for 12 ML and to 0.267 eV⁻¹ for 15 ML. As a consequence, we obtain from Eq. (1) for the exchange coupling constant

$$J \approx 0.32 \pm 0.04 \text{ eV}.$$

As compared to semiconductor bulk systems,²³ the value of J is two to four times smaller, which is not surprising because the coupling to a surface, in general, is much weaker than the coupling within the bulk.

Due to the logarithmic dependence on T_K , the determined value of J is particularly insensitive to experimental inaccuracies. The outcome of our fitting procedure is displayed in Fig. 2. As to be expected, the dependence of T_K on the film thickness largely resembles the behavior of ρ (see the bottom of Fig. 1). We do not find indications of a dependence of the exchange coupling constant J on the film thickness between 11 and 18 ML. Hence, there is a qualitative agreement with

the experimental results even though clarification of the 1 ML shift and T_K spike at 17 ML should be tackled by future experiments.

In summary, we have performed first-principles calculations to establish the density of states of Pb(111) films grown on a Si(111) substrate. These *ab initio* data have enabled us to fit experimental results from measurements addressing the

dependence of the Kondo temperature on the Pb film thickness. In particular, we have succeeded in calculating the exchange coupling constant J , which is not accessible to direct experimental determination. For the system under investigation, a value of about $J=1/3$ eV transpires.

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- ¹A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, 1993).
- ²H. O. Frota and L. N. Oliveira, Phys. Rev. B **33**, 7871 (1986).
- ³V. L. Campo, Jr. and L. N. Oliveira, Phys. Rev. B **68**, 035337 (2003).
- ⁴D. Goldhaber-Gordon, H. Shtrikman, D. Mahalu, D. A. Magder, U. Meirav, and M. A. Kastner, Nature (London) **391**, 156 (1998).
- ⁵S. M. Cronenwett, T. H. Oosterkamp, and L. P. Kouwenhoven, Science **281**, 540 (1998).
- ⁶F. Simmel, R. H. Blick, J. P. Kotthaus, W. Wegscheider, and M. Bichler, Phys. Rev. Lett. **83**, 804 (1999).
- ⁷M. Krawiec and K. I. Wysokiński, Phys. Rev. B **66**, 165408 (2002).
- ⁸A. C. Seridonio, F. M. Souza, and I. A. Shelykh, J. Phys.: Condens. Matter **21**, 095003 (2009).
- ⁹V. Madhavan, W. Chen, T. Jamneala, M. F. Crommie, and N. S. Wingreen, Science **280**, 567 (1998).
- ¹⁰N. Knorr, M. A. Schneider, L. Diekhöner, P. Wahl, and K. Kern, Phys. Rev. Lett. **88**, 096804 (2002).
- ¹¹K. Nagaoka, T. Jamneala, M. Grobis, and M. F. Crommie, Phys. Rev. Lett. **88**, 077205 (2002).
- ¹²P. Wahl, L. Diekhöner, G. Wittich, L. Vitali, M. A. Schneider, and K. Kern, Phys. Rev. Lett. **95**, 166601 (2005).
- ¹³A. Schiller and S. Hershfield, Phys. Rev. B **61**, 9036 (2000).
- ¹⁴M. Plihal and J. W. Gadzuk, Phys. Rev. B **63**, 085404 (2001).
- ¹⁵O. Újsághy, J. Kroha, L. Szunyogh, and A. Zawadowski, Phys. Rev. Lett. **85**, 2557 (2000).
- ¹⁶Y.-S. Fu, S.-H. Ji, X. Chen, X.-C. Ma, R. Wu, C.-C. Wang, W.-H. Duan, X.-H. Qiu, B. Sun, P. Zhang, J.-F. Jia, and Q.-K. Xue, Phys. Rev. Lett. **99**, 256601 (2007).
- ¹⁷C. M. Wei and M. Y. Chou, Phys. Rev. B **66**, 233408 (2002).
- ¹⁸V. Eyert, *The Augmented Spherical Wave Method: A Comprehensive Treatment*, Lecture Notes in Physics Vol. 719 (Springer, Heidelberg, 2007).
- ¹⁹U. Schwingenschlögl, V. Eyert, and U. Eckern, Europhys. Lett. **61**, 361 (2003).
- ²⁰U. Schwingenschlögl and C. Schuster, J. Phys.: Condens. Matter **20**, 382201 (2008); EPL **81**, 17007 (2008).
- ²¹U. Schwingenschlögl, R. Frésard, and V. Eyert, Surf. Sci. **603**, L19 (2009).
- ²²P. Czoschke, H. Hong, L. Basile, and T.-C. Chiang, Phys. Rev. B **72**, 075402 (2005).
- ²³T. Mizokawa and A. Fujimori, Phys. Rev. B **56**, 6669 (1997).