

Influence of hydrogen impurities on atomic and electronic structure of palladium nanowires and nanocontacts

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We present an *ab initio* study of the influence of hydrogen impurities (atoms and molecules) on the atomic structure and electronic properties of Pd nanowires and atomic-size nanocontacts. Various atomic positions for hydrogen adsorption within palladium structures are considered. It is found that adsorbed hydrogen can penetrate into the atomic structure of Pd nanocontacts and nanowires and by that increase their stability close to and beyond their breaking points. The interaction between hydrogen and palladium atoms alters the interatomic bonding and hybridization of electronic states of palladium atoms. The interaction of palladium with hydrogen leads to the suppression of magnetic properties of Pd nanowires and nanocontacts. Additionally, the possibility of dissociation of molecular hydrogen at palladium nanocontacts is discussed, which is an important issue for catalytic applications.

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I. INTRODUCTION

A major milestone on the way to miniaturizing electronic devices is achieving low dimensionality of exploited structures. At this point classical size reduction meets with electronic and magnetic quantum effects, which opens a wide range of new scientific and engineering options. A good example of such a low-dimensional nanostructure is a metallic nanowire (NW) or a nanocontact (NC). Such wires and contacts can be relatively easily created by the mechanically controllable break junction (MCBJ) technique or, if greater precision is needed, by manipulating single atoms at surfaces with a scanning tunneling microscope (STM) tip (see, e.g., Refs. 1–3). But most importantly, quantum effects in metallic NWs can be exploited without resorting to cryogenic temperatures. Thus it is not surprising that low-dimensional structures have been an active research area over the past years.^{1–22} It was shown that nanowires exhibit ballistic electronic transport with the conductance close to its one-dimensional quantum limit $G_0 = 2e^2/h$.^{1–4} Further intensive experimental studies of nanowires demonstrated unexpectedly that a NW's conductance can also exhibit half-integer values at room temperatures.^{1,4} It has been assumed that such deviation from integer values could be the result of contamination with gas impurities (H, C, O, H₂, O₂, etc.). Production of delicate low-dimensional nanostructures requires ultrahigh vacuum conditions, but gas impurities are hard to avoid completely. The influence of gas impurities on atomic and electronic structures has been widely studied experimentally and theoretically.^{6–13} These studies have confirmed that insertion of impurity atoms or molecules into a metal contact results in a significant change of the NC's atomic and electronic structures. Besides, the interaction with impurity atoms and molecules can strongly affect the stability of nanocontacts.^{11–13} Kiguchi *et al.* have found that palladium NCs can be bridged by impurities which enhances their stability close the classical breaking point. This study has been performed in a solution using an electrochemical scanning tunneling microscope (EC-STM).¹¹ Skorodumova and

coworkers, on the contrary, have observed, in their theoretical study, that gold nanocontacts are destabilized and subsequently destroyed by impurity molecules and atoms of light gases (H, C).¹² Csonka *et al.* have investigated experimentally Pd and Pt NCs in the presence of hydrogen by means of STM. They have observed the formation of a new peak in conductance histograms for these nanocontacts in hydrogen atmosphere.¹³ Thus it has been demonstrated that hydrogen, among other impurities, can have a strong effect on both the atomic structure and electronic properties of nanowires and nanocontacts. The interaction between hydrogen impurities and one-dimensional structures is especially interesting in the case of magnetic NWs and NCs of *d* elements.

The occurrence of magnetism and its effect on quantized transport in different 3*d*, 4*d*, and 5*d* transition metal NCs and NWs have been extensively explored both experimentally¹ and theoretically.^{11,13,23} Yet magnetic properties of those nanojunctions are still under debate for a whole class of 4*d* and 5*d* elements, e.g., palladium, which are normally nonmagnetic.^{23–36} Palladium, for example, can exhibit magnetic properties in low-dimensional structures, whereas the bulk of palladium is paramagnetic. In a series of experimental works freestanding palladium nanoclusters, nanoparticles (24 nm), and surfaces have been shown to exhibit magnetic properties.^{37–41} The investigation of magnetic properties of one-dimensional Pd structures was continued in several theoretical works.^{23–29,42} In these works the existence of magnetic properties in Pd NWs and NCs was confirmed. Still, the topic has been a source of much controversy. For example, it was debated by Delin *et al.*^{28,43} and Alexandre *et al.*⁴⁴ whether the density functional theory in local density (LDA) or generalized gradient (GGA) approximations was a more appropriate tool for the description of magnetic properties of nanocontacts and nanowires, thus raising doubts as to the validity of the prediction of magnetic properties. In our recent paper²⁷ we have shown that while the choice between LDA and GGA might affect the precise quantitative value of the magnetic

moment the crucial role in determining magnetic properties is played by the atomic structure of a nanocontact or a chain. In our further publication⁴⁵ we have shown that single hydrogen atoms can have a decisive effect on both structural and, most importantly, magnetic properties of low-dimensional Pd nanostructures.

In the present paper we would like to extend our previous investigations^{27,45} with a comprehensiveab initiostudy of the influence of hydrogen impurities (single atoms and molecules) on atomic, electronic, and above all magnetic properties of palladium nanocontacts and nanowires. With our state-of-the-art first-principles calculations of magnetic properties of infinite Pd NWs and atomic-sized Pd NCs in the presence of hydrogen impurities we demonstrate that single hydrogen atoms and hydrogen molecules can significantly affect the stability and magnetic properties of one-dimensional Pd systems. Besides registering phenomenological changes we point out underlying fundamental electronic structure features and connections.

II. METHOD

Our self-consistent electronic-structure calculations of Pd wires and atomic-sized contacts have been performed by means of the projector augmented wave (PAW) technique⁴⁶ as implemented in the Vienna Ab initio Simulation Package (VASP) code,^{47–49} which is based on the density functional theory (DFT). Calculations presented in this paper were based on the self-consistent Kohn-Sham equations.^{47–49} Electronic states were described using the basis of plane waves. The cutoff energy for the plane wave basis of 250 eV was used. The generalized gradient approximation (GGA) for the exchange-correlation functional has been applied. We used for calculations the PAW pseudopotentials using the Perdew-Wang '91 treatment,⁵⁰ to study the influence of the hydrogen impurity atoms and molecules on the magnetic properties of infinite Pd wires and nanocontacts. A structural relaxation was performed via a quasi-Newton algorithm, using the exact Hellmann-Feynman forces acting on each atom. The total energies of the system were converged up to 1 meV/atom, while the residual force acting on each atom was less than 0.01 eV/Å. The integration over the Brillouin zone (BZ) was performed using the tetrahedron method with Blöchl corrections.⁵¹ The structure of Pd NWs has been represented by means of a three-dimensional supercell with periodic boundary conditions. The Pd wire was represented by an atomic chain aligned along the z axis separated from its images along the x and y directions (10 Å) to avoid spurious interactions with them. A one-dimensional Brillouin zone was used, along the z axis of the wire. BZ sampling was performed using a $1 \times 1 \times 7$ k -point mesh in a Monkhorst-Pack grid.⁵² Our calculations of the total energy with a different k -point mesh ($1 \times 1 \times 4$, $1 \times 1 \times 6$, $1 \times 1 \times 7$, $1 \times 1 \times 8$, $1 \times 1 \times 9$) have shown that a $1 \times 1 \times 7$ k -point mesh was sufficient to study the electronic and structural properties of Pd nanowires. Further extension of the k -point mesh did not increase the accuracy of the total energy calculations. In order to study the atomic structure and electronic properties of Pd NCs we used the model of palladium contact suggested by Matsuda and Kizuka.⁵ According to this model the Pd

nanocontact is represented in our work as the three-atomic Pd chain suspended in vacuum between two Pd electrodes. Pd electrodes were modeled as 5 Pd monolayers. The electrodes are separated from one another by a vacuum layer large enough in the z direction (10 Å) to exclude any interaction between electrodes. The size of the supercell along the x and y directions was chosen sufficiently large (10 Å) to avoid the interaction between the NC's chain and its image. Our total energy calculations have shown that a k -point set $4 \times 4 \times 1$ is efficient to study the electronic and structural properties of Pd nanocontacts.

III. RESULTS AND DISCUSSION

A. Nanowires

The main aim of the present study was to determine how the magnetism and structure of Pd nanocontacts and nanowires can be affected if single hydrogen atoms and molecules are adsorbed on them. Let us first consider the adsorption of a single H atom on a monatomic Pd nanowire as an idealized model of a very long nanocontact's chain. This model allows one to study the interaction between Pd and H atoms in the wire and to ignore the interaction with electrodes, which are inevitably present in a real system.

We have studied several possible configurations of a NW with different adsorption positions of the hydrogen atom (Fig. 1): (a) The hydrogen atom is situated close to a palladium atom of the wire (configuration called “aside”); (b) the hydrogen atom resides in the vicinity of the Pd wire between two Pd atoms (“middle”); (c) the hydrogen atom is embedded into the nanowire (“linear” configuration). Calculations have been performed for a wide range of interatomic distances between Pd atoms in the wire (from 2.4 Å to 3.0 Å).⁵³ This range, according to our previous paper on the subject,²⁷ corresponds to the maximal value of magnetic moment in a pure Pd NW. The equilibrium interatomic distance for a pure Pd NW is 2.44 Å. Our calculations have shown that the distance between the hydrogen and palladium atoms remains practically unchanged upon stretching or contracting the NW (relatively rigid bond) for the aside and middle configurations. For the aside configuration the Pd-H distance exactly matches

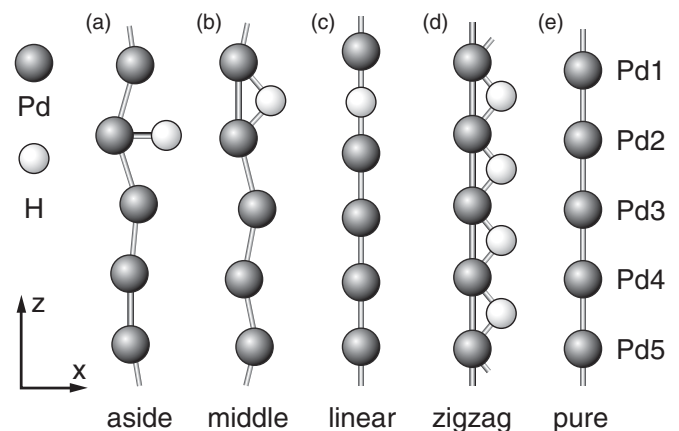


FIG. 1. Studied adsorption positions of hydrogen atoms (light balls) in an infinite Pd (dark balls) nanowire: (a) “aside,” (b) “middle,” (c) “linear,” (d) “zigzag,” and a “pure” Pd nanowire (e).

TABLE I. Difference of total energy values E (in eV) for considered adsorption positions of hydrogen atom in Pd nanowire at interatomic distances 2.7 Å and 3.0 Å. The energy values are set relative to the energy of the most stable configuration.

$d_{\text{Pd-Pd}}$	Middle	Alongside	Linear	Pure
2.7	0.00	0.27	0.30	4.27
3.0	0.03		0.00	4.31

the equilibrium distance in a Pd-H dimer (~ 1.55 Å). In the middle configuration equilibrium distances between Pd and H atoms are slightly larger, ~ 1.72 Å. As expected, total energy calculations have shown that for contracted NWs the energetically preferable configuration is the middle one, as the hydrogen seeks to maximize the number of neighbors. If the NW is stretched beyond ~ 3 Å the hydrogen incorporates into the chain and the linear configuration becomes energetically more preferable. According to our previous calculations, the distance between palladium atoms of 3.0 Å roughly corresponds to the breaking point of a pure palladium nanowire.⁴⁵ We thus see that hydrogen can act as a bridge stabilizing the nanowire at large interatomic distances (>3.0 Å). Our earlier calculations have shown that for all considered configurations Pd NWs break upon stretching at Pd-Pd rather than at Pd-H bonds.⁴⁵ In Table I we compare the system's total energies in various adsorption configurations for two interatomic distances: 2.7 Å (corresponds to the maximum value of local magnetic moments of Pd atoms in a pure nanowire)²⁷ and 3.0 Å (corresponds to the breaking point of a pure Pd wire). For the interatomic distance of 2.7 Å the total energies of linear and aside configurations are 0.3 eV larger than the total energy of the middle configuration. As the NW is stretched, the total energy difference between the linear and the middle configurations decreases until at ~ 2.8 Å those configurations become equally favorable. Finally, at 3.0 Å the linear configuration has a 0.03 eV smaller total energy. Since Pd has a high affinity with hydrogen, we studied additionally the interaction of palladium NWs with multiple hydrogen atoms. This configuration was modeled using the "zigzag" configuration as shown in Fig. 1(d). Hydrogen atoms were placed close to the nanowire between Pd atoms. This configuration of H adsorption was found to be energetically most preferable. Our previous calculations have shown that due to the interaction with hydrogen atoms the zigzag configuration displays the largest values of cohesive energies in the whole range of interatomic distances.⁴⁵ Similar to the case of a single H adsorbate, the zigzag configuration morphs into a linear structure upon stretching as the hydrogens embed into the chain of the Pd wire. Thus the chain retains its stability at even larger Pd-Pd separations.

Let us now turn to the influence of hydrogen adsorption on magnetic properties of palladium nanowires. As a reference we shall use an "ideal" (clean) Pd chain [Fig. 1(e)]. As discussed in our previous studies on the subject^{27,45} such NWs without hydrogen impurities show magnetic properties in a wide range of interatomic distances (local magnetic moment of a single Pd atom as a function of interatomic distance is shown in Fig. 2 with black circles). The cause for this onset

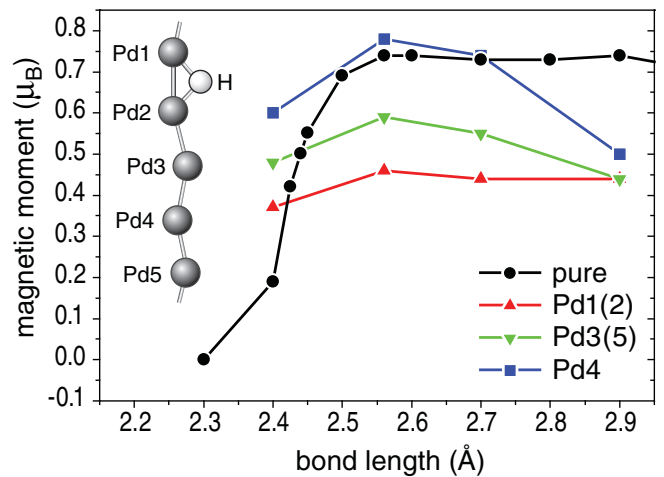


FIG. 2. (Color online) Change of the local magnetic moments of Pd atoms as a function of interatomic distance for a pure nanowire (black circles) (Ref. 27) and for atoms Pd1 (red up-triangles), Pd2 (green down-triangles), and Pd3 (blue squares) of a nanowire with an adsorbed hydrogen atom ("middle" configuration) (solid lines).

is obviously the reduced dimensionality of the system. This, nevertheless curious, phenomenon (occurrence of magnetism in nanowires of nonmagnetic materials) has been discussed widely, with an accent on their electronic structure.^{24,25,54} Roughly speaking, as the chain is stretched, the interatomic interaction is weakened and the bands become narrower and shift to higher energies. As the band edges cross the Fermi level, van Hove singularities at band edges abruptly increase the electron density at the Fermi level, thus favoring magnetism in the spirit of the Stoner criterion.

It would thus be conceivable that the influence of hydrogen on the electronic structure could also have a considerable effect on magnetism. We have studied the interaction of hydrogen with Pd wires in the most stable middle configuration. Spin-polarized calculations have shown that magnetic moments of Pd atoms closest to hydrogen [Pd1 and Pd2 in Fig. 1(b)] are significantly decreased (to about $0.4 \mu_B$), while the local magnetic moments of remote atoms (Pd3, Pd4, and Pd5) remain at a value of approximately $0.7 \mu_B$ as in a pure Pd NW (Fig. 2). Such inhomogeneous distribution in local magnetic moments of Pd atoms is caused by the difference in interaction of Pd atoms with the hydrogen. Strong interaction with the nearest neighbors causes much larger changes in their electronic structure.

In order to get a better understanding of how hydrogen quenches magnetism in Pd we study in more detail its influence on the electronic properties of the NW. In Fig. 3 the non-spin-resolved PDOS of Pd atoms of the chain in the middle configuration is presented. The DOS of Pd atoms weakly interacting with the hydrogen [Pd3 (Pd5) and Pd4, Figs. 3(b) and 3(c), respectively] has electronic structure which is virtually identical with that of a pure NW. However, the electronic structure of palladium atoms nearest to H [Pd1(2), Fig. 3(a)] is significantly different. Formation of a new narrow hybrid band between s and d_{z^2} , d_{xz} states of H and Pd, respectively, at about -4.6 eV can be observed. The positions of hydrogen atomic s states are marked on the graphs by red arrows. The bands closer to the Fermi

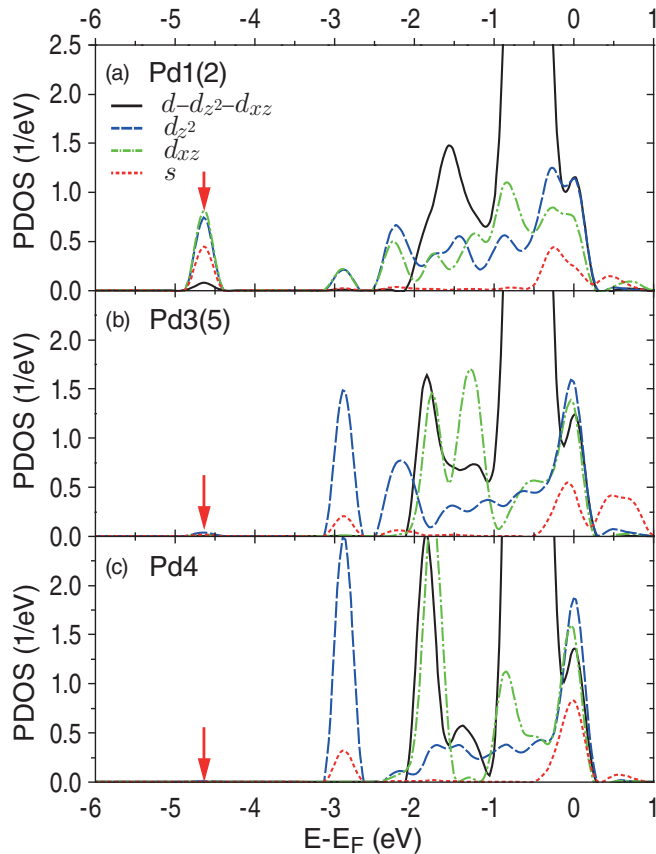


FIG. 3. (Color online) PDOS of palladium atoms in nanowire in presence of hydrogen impurities for “middle” configuration at interatomic distance 2.7 Å. Red arrows mark the positions of low-energy levels of the hydrogen atom.

level are significantly broadened and the electron density at the Fermi energy is visibly reduced. This transformation of the density of states is to a large extent due to the changes in the bonding geometry. Indeed, the bonding angles in the middle configuration are different for the atoms neighboring the hydrogen and those farther away from it. The latter are close to the linear geometry. This geometry determines the symmetry of the orbitals participating in the bonding. All in all, the broadening of the band and the reduction of the electron density at the Fermi energy lead to the reduction of the spin-polarization and the quenching of the magnetism.

We can thus say that insertion of hydrogen atoms into a Pd wire is, on the one hand, energetically preferable and leads to an increased stability of the wire. On the other hand, as a result of interaction between hydrogen and palladium atoms the magnetic properties of the Pd NW are strongly suppressed.

B. Nanocontacts

In the next stage of our work we would like to extend our study to the case of more realistic systems, namely Pd nanocontacts (NCs). Here we also considered several possible configurations of hydrogen adsorption (Fig. 4). The NCs were always modeled as pyramids consisting of 5 Pd atoms (we shall call them the “leads”). The apex atoms were considered to belong to the “chain” of the nanocontact. The whole chain

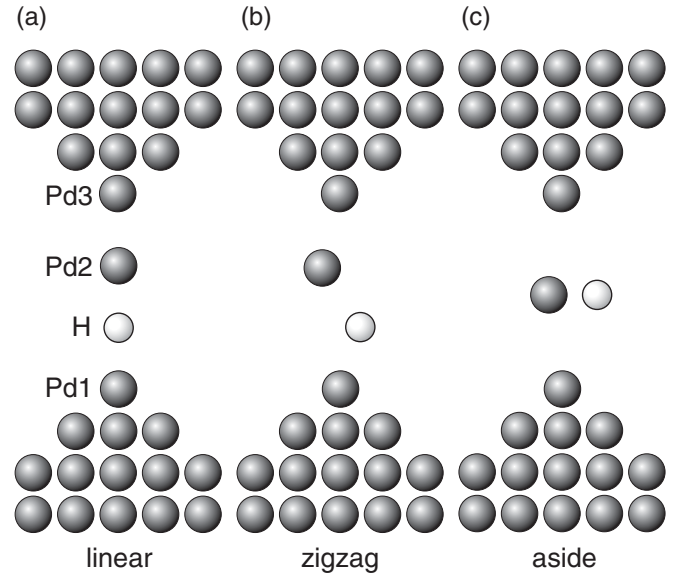


FIG. 4. Available adsorption positions of hydrogen atom in Pd nanocontacts: (a) “linear” configuration, (b) “zigzag” configuration, (c) “aside” configuration.

consisted of two apex atoms (Pd1 and Pd3 in Fig. 4) and a Pd atom placed between them (Pd3).⁵⁵ The hydrogen atom was placed either into the chain of the nanocontact (linear configuration), beside the chain in between Pd1 and Pd2 (zigzag) or abreast of the middle Pd3 atom (aside). Those geometries are sketched in Figs. 4(a), 4(b), and 4(c), respectively. We have studied the adsorption of the hydrogen atom in Pd NC for several interelectrode distances ranging from 8.43 Å to 9.7 Å (the distance is given as the separation between the four-atomic bases of the contacts), which corresponds to the range where Pd NCs show magnetic properties, according to our previous work.²⁷ Our total energy calculations have shown that the zigzag configuration is energetically preferable for contracted palladium nanocontacts. If the NC is stretched, the hydrogen atom incorporates into the NC’s chain which is well illustrated by the decrease of the difference of total energies between in-wire and zigzag configurations for large interelectrode distances (>9.7 Å). The trend is shown in Fig. 5.

Let us now come to the influence of hydrogen impurity atoms on magnetic properties of Pd NCs. Our calculations have shown that the electronic structure of nanocontacts also significantly changes in the presence of hydrogen impurities (Fig. 6). The LDOS of Pd1 and Pd2 atoms [numbering according to Fig. 4(a)] in the presence of hydrogen [top panels in Figs. 6(a) and 6(b), respectively] differs from the DOS of pure palladium nanocontacts (bottom panels in Fig. 6). If we compare the LDOSs of clean contacts and contacts with hydrogen adsorbed we find that while both Pd1 and Pd2 are significantly affected by the hydrogen, Pd1 retains more features of the clean NC even when it is brought into contact with hydrogen. This shows that Pd1 is still tightly bound to the underlying contact (the 4 Pd atoms making up the base of the nanocontact’s tip) and Pd2. Pd2, on the contrary, has only two immediate Pd neighbors (Pd1 and Pd3). It is thus more susceptible to the influence of hydrogen (as

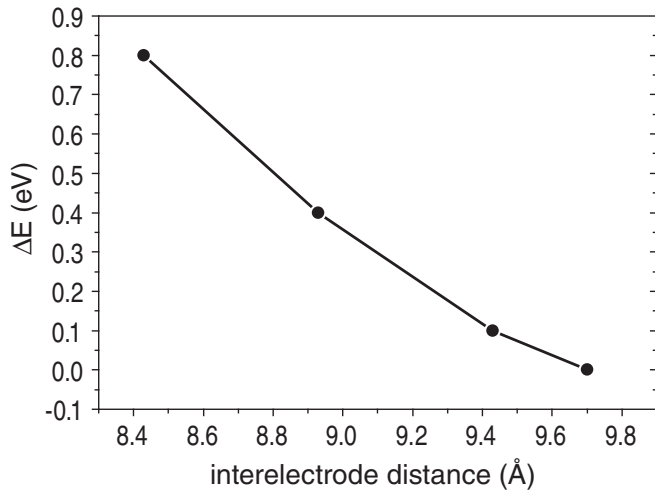


FIG. 5. The difference of total energy (ΔE) of “linear” and “zigzag” configurations as a function of the interelectrode distance.

can clearly be inferred from Fig. 6). For both cases a major feature is once again the hybridization of palladiums s and d orbitals with hydrogen electronic levels (the peaks at -5 and -3.5 eV). Besides, not unlike in Pd nanowires, the geometry of a nanocontact is significantly distorted (Fig. 4). Both those factors lead to the broadening of the bands and their shift to lower energies. As a consequence, the population at the Fermi energy is palpably reduced [Fig. 6(a)]. This has the consequence that magnetism is strongly suppressed within the NC’s chain. Figure 7 vividly illustrates this fact. Local magnetic moments of Pd atoms are plotted in Fig. 7 versus the intercontact distance for the cases of a clean Pd NC (hollow black circles for Pd2 and hollow red squares for Pd1, Pd3) and a NC with H adsorbed (filled markers: blue triangles pointing down [Pd1], cyan circles [Pd2], and green triangles pointing up [Pd3]). The strength of the interaction with hydrogen can be also clearly traced here. The local magnetic moment of the central Pd atom is decreased almost tenfold in the presence of hydrogen (from $0.36 \mu_B$ to $0.04 \mu_B$). Local magnetic moments

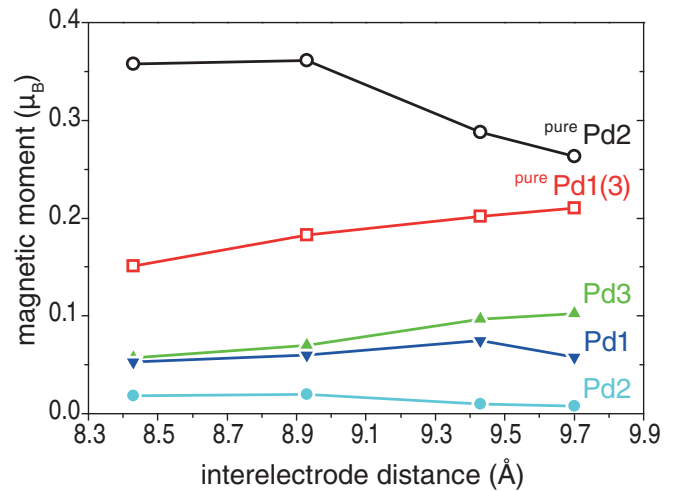


FIG. 7. (Color online) Dependence of the local magnetic moments of Pd atoms in nanocontact’s chain on interelectrode distances for pure Pd nanocontact (dot lines) and for Pd nanocontact with the hydrogen atom (“zigzag” configuration) (solid lines).

of the edge Pd atoms are also significantly decreased, though not so drastically, because they retain the interaction with the leads. Thus the calculations have demonstrated that due to the interaction between Pd atoms of the nanocontact’s chain and the hydrogen atom the magnetic properties of the Pd nanocontact in whole are practically suppressed. This is bound to have an effect on conductance properties of the junction.

C. Hydrogen molecules

To cover another example of a realistic experimental scenario, we have also considered the interaction of palladium nanocontacts with hydrogen molecules. This was largely motivated by recent experimental work of Csonka *et al.* in which the strong influence of hydrogen impurities on transport properties of Pd NCs has been observed. They have observed the formation of a new peak in conductance

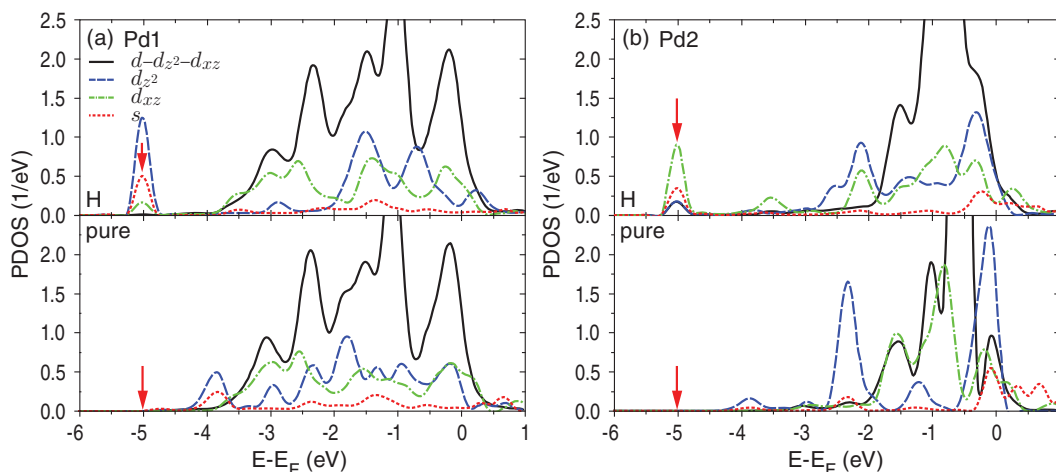


FIG. 6. (Color online) PDOS of Pd atoms in the nanocontact’s chain in “zigzag” configuration: (a) edge atom (Pd1) and (b) central atom (Pd2). Top panels present the PDOS in presence of hydrogen atom while the bottom ones present pure NC’s PDOS for comparison. Vertical arrows mark the positions of low-energy s states of the hydrogen atom.

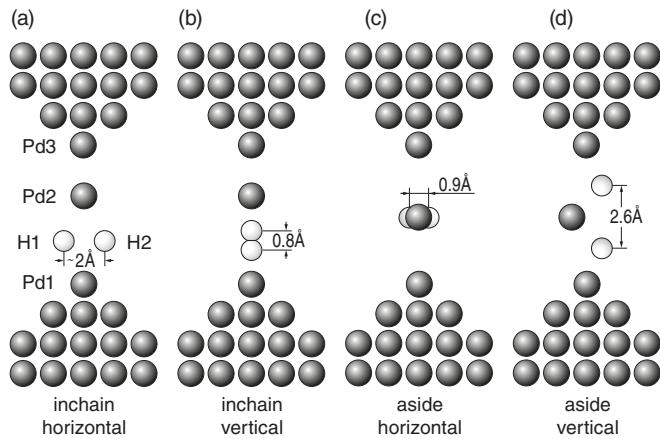


FIG. 8. Available adsorption positions of the hydrogen molecule in palladium nanocontacts: (a) “in-chain horizontal,” (b) “in-chain vertical,” (c) “aside horizontal,” and (d) “aside vertical.”

histograms of Pd nanocontacts in hydrogen atmosphere.⁵⁶ To explain the phenomenon they have reasoned that an H_2 bridge might have been formed in the chain of the nanocontact. They proposed two different possible positions of the H_2 molecule in the contact: “in-chain horizontal” [Fig. 8(a)] and “in-chain vertical” [Fig. 8(b)], yet no detailed analysis of mechanical and electronic properties of those configurations was given. In the present section we want to consider in detail the atomic structure and electronic properties of both configurations mentioned above. In addition we propose two more configurations, which should cover the likely possibility that the molecule is not incorporated into the chain, but rather takes its place alongside the chain of the NC. Those configurations are sketched in Figs. 8(c) and 8(d). We shall call them respectively “aside horizontal” and “aside vertical.”

Our calculations have shown that the formation of the H_2 bridge (configuration “in-chain vertical”) becomes energetically preferable for stretched Pd contacts with interelectrode distances above 9.7 Å. According to Matsuda *et al.*⁵ this separation is beyond the breaking point for such a contact

in the absence of hydrogen contamination. This shows that Pd NCs (as well as Pd NWs) are stabilized by hydrogen molecules far beyond their classical breaking point. For contracted NC (interelectrode distances less than 9.7 Å) the bridge (in-chain vertical) configuration becomes stressed and cannot sustain its linear shape. Therefore the H_2 molecule is expelled from the contact’s chain but remains adsorbed at the side of the NC’s chain [Figs. 8(c) and 8(d)]. Our results agree well with the recent experimental work by Kiguchi *et al.*⁵⁷ where the authors have found experimentally that the hydrogen bridge can be formed only for stretched Pd nanocontacts. According to our previous work pure Pd nanocontacts would exhibit magnetic properties at 9.7 Å interelectrode separation.²⁷ The local magnetic moment of the central atom in this case was found to be about $0.2 \mu_B$. Introducing a hydrogen molecule into the system would thus allow us to study the influence of hydrogen molecules not only on structural stability but also on magnetic properties of palladium contacts.

We know now that the adsorption of a H_2 molecule can stabilize Pd NCs at large interelectrode distances. There is, however, another intriguing feature: In certain configurations the interaction strength between Pd and H is strong enough to break the molecular bond in H_2 and thus lead to the molecule’s dissociation. Let us elaborate a bit more on this possibility. The first indication of the molecule’s dissociation is the increase of the bond length (0.75 Å in a freestanding molecule) to more than 2 Å as can be observed for the in-chain–horizontal and aside–vertical configurations [Figs. 8(a) and 8(d)]. A much more conclusive proof, however, can be found in the analysis of the hydrogen’s molecular states. In Fig. 9 the PDOS of hydrogen atoms in the configurations sketched in Fig. 8 are presented (panels labeled with corresponding letters and configuration names). To determine whether the molecule dissociates we shall compare the PDOSs of Pd atoms nearest to the adsorbed molecules with the electronic levels of a freestanding H_2 .¹⁷ Looking at the electronic structures of H_2 adsorbed at a Pd NC in the in-chain–horizontal and aside–vertical configurations [Figs. 9(a) and 9(d)] we can clearly identify peaks lying at about -5 eV as belonging to

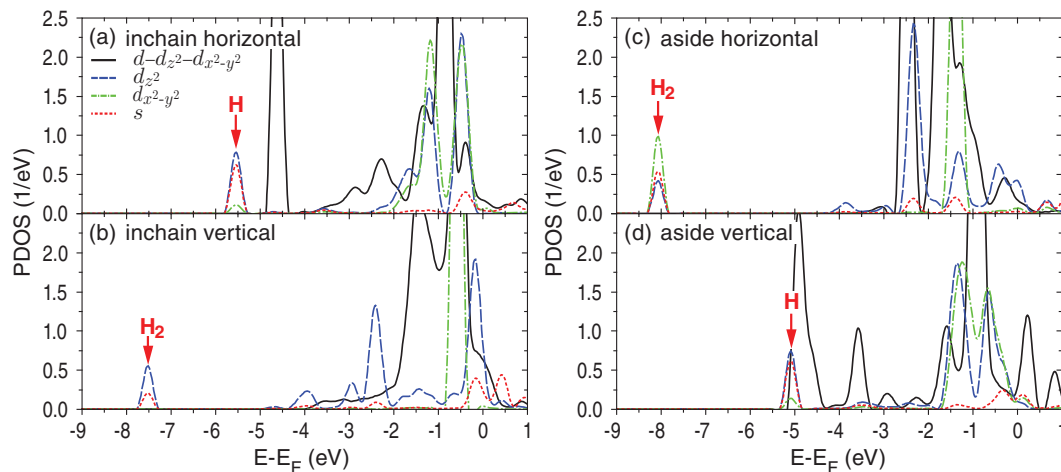


FIG. 9. (Color online) PDOS of Pd atoms nearest to the H_2 molecule adsorbed on a Pd NC in different positions: (a) “in-chain horizontal,” (b) “in-chain vertical,” (c) “aside horizontal,” and (d) “aside vertical.” Red arrows mark the position of low-energy (bonding) states of H/H_2 .

atomic hydrogen rather than to an H_2 molecule. The remaining two configurations [Figs. 9(b) and 9(c)] exhibit deeper lying states (around -8 eV) that can be attributed to a bonded hydrogen molecule. In Fig. 9 the most prominent molecular and atomic states are marked by red arrows. Obviously, since both the H_2 molecule and single H atoms interact, however slightly, with each other and with the chain, the total number of molecular and atomic states by far exceeds one. Here, however, we will not mark them all on the graph but rather focus on one of them for clarity. The variation in the position of both atomic and molecular states gives us a rough estimate of the degree to which the molecule or atom is bound to the chain (or, in the case of the molecule, of the molecular bonding). Now we have a clear proof that molecular states of the H_2 in the in-chain–horizontal and aside-vertical configurations are not formed, which means that the H_2 molecule would dissociate on a Pd NC, if adsorbed in those configurations. In the in-chain–vertical and aside-horizontal configurations [Figs. 8(b) and 8(c)] the bond length of the hydrogen molecule is equal to a slightly stretched (respectively compressed) free hydrogen molecule. It can also be noted that the energetically unfavorable compression of the molecule is accompanied by an upward shift of the molecular level.

According to our total energy calculations, it is energetically preferable for a hydrogen molecule adsorbed on the chain of a Pd NC to dissociate. The difference of total energies between the in-chain–horizontal and aside-vertical configurations and the in-chain–vertical and aside-horizontal configurations is of the order of 1 eV. Our results agree well with the experimental work by Kiguchi *et al.*⁵⁷ in which it was also found that the hydrogen molecule easily dissociates on a chain of a short Pd nanocontact. They have also observed two vibrational modes for Pd nanocontacts in the hydrogen atmosphere, which correspond to different atomic configurations of the Pd nanocontact. Our calculations hint that those two stable configuration might be the in-chain–horizontal and aside-vertical ones, as they have the lowest total energies. It can be noted also that other well-known examples exist, where the high affinity of biatomic gas molecules to metals leads to their dissociation. As an example dissociation of H_2 , O_2 , and CO_2 at Pt surfaces and protruding step edges

can be given.^{58–60} This is an effect of major importance in the field of catalysis.

For the sake of completeness we shall also mention the magnetic properties of Pd NC in the presence of molecular (or dissociated) hydrogen. As might be expected, our calculations have shown that the magnetism of Pd is strongly suppressed by the interaction with the hydrogen. Local magnetic moments of Pd atoms are strongly decreased (to about $0.1 \mu_B$) for all considered configurations. The underlying physics in terms of the electronic structure is strictly analogous to the case of a single H atom adsorption.

IV. SUMMARY AND CONCLUSION

To sum up, our study has provided clear evidence, based on the analysis of the electronic structure, that the insertion of hydrogen atoms into palladium nanowires can stabilize the wire beyond its breaking point, as the hydrogen atom embeds into the nanowire when the latter is stretched. We have shown that the strong interaction of hydrogen atoms with palladium can cause reduction of the spin polarization in the system and suppression of its magnetic properties. Our calculations demonstrate that local magnetic moments of Pd atoms in the nanowire decrease from $0.7 \mu_B$ (in pure Pd nanowire) to $0.4 \mu_B$ in the presence of hydrogen impurity atoms. Similar trends have been evidenced for realistic palladium nanocontacts. The interaction with the hydrogen molecule strongly changes the electronic structure of Pd nanocontacts. Total energy calculations have shown that the formation of a vertical conductivity “hydrogen bridge” in the chain of Pd nanocontacts is possible only for stretched ones with interelectrode distances of 9.7 \AA . The dissociation of hydrogen molecules in a chain of nanocontacts is only possible in contracted Pd contacts. The interaction of the hydrogen molecule with palladium nanocontacts causes suppression of their magnetic properties.

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¹V. Rodrigues, J. Bettini, P. C. Silva, and D. Ugarte, *Phys. Rev. Lett.* **91**, 096801 (2003).

²C. Untiedt, A. I. Yanson, R. Grande, G. Rubio-Bollinger, N. Agrait, S. Vieira, and J. M. van Ruitenbeek, *Phys. Rev. B* **66**, 085418 (2002).

³A. I. Yanson, G. R. Bollinger, H. E. van den Brom, N. Agrait, and J. M. van Ruitenbeek, *Nature (London)* **395**, 783 (1998).

⁴R. H. M. Smit, C. Untiedt, G. Rubio-Bollinger, R. C. Segers, and J. M. van Ruitenbeek, *Phys. Rev. Lett.* **91**, 076805 (2003).

⁵T. Matsuda and T. Kizuka, *Jpn. J. Appl. Phys.* **46**, 4370 (2007).

⁶N. V. Skorodumova and S. I. Simak, *Phys. Rev. B* **67**, 121404 (2003).

⁷N. V. Skorodumova, S. I. Simak, A. E. Kochetov, and B. Johansson, *Phys. Rev. B* **72**, 193413 (2005).

⁸A. Grigoriev, N. V. Skorodumova, S. I. Simak, G. Wendin, B. Johansson, and R. Ahuja, *Phys. Rev. Lett.* **97**, 236807 (2006).

⁹S. R. Bahn, N. Lopez, J. K. Nørskov, and K. W. Jacobsen, *Phys. Rev. B* **66**, 081405 (2002).

¹⁰P. Jelínek, R. Pérez, J. Ortega, and F. Flores, *Phys. Rev. Lett.* **96**, 046803 (2006).

¹¹M. Kiguchi and K. Murakoshi, *Appl. Phys. Lett.* **88**, 253112 (2006).

¹²N. V. Skorodumova, S. I. Simak, A. E. Kochetov, and B. Johansson, *Phys. Rev. B* **75**, 235440 (2007).

¹³S. Csonka, A. Halbritter, and G. Mihály, *Phys. Rev. B* **73**, 075405 (2006).

- ¹⁴K. Terabe, T. Hasegawa, T. Nakayama, and M. Aono, *Nature (London)* **433**, 47 (2005).
- ¹⁵J. Bettini, F. Sato, P. Z. Coura, S. O. Dantas, D. Galvão, and D. Ugarte, *Nature Nanomater.* **1**, 182 (2006).
- ¹⁶H. Ohnishi, Y. Kondo, and K. Takayanagi, *Nature (London)* **395**, 780 (1998).
- ¹⁷Y. Takai, T. Kawasaki, Y. Kimura, T. Ikuta, and R. Shimizu, *Phys. Rev. Lett.* **87**, 106105 (2001).
- ¹⁸U. Landman, W. D. Luedtke, B. E. Salisbury, and R. L. Whetten, *Phys. Rev. Lett.* **77**, 1362 (1996).
- ¹⁹V. Rodrigues and D. Ugarte, *Phys. Rev. B* **63**, 073405 (2001).
- ²⁰V. M. García-Suárez, A. R. Rocha, S. W. Bailey, C. J. Lambert, S. Sanvito, and J. Ferrer, *Phys. Rev. Lett.* **95**, 256804 (2005).
- ²¹V. M. García-Suárez, A. R. Rocha, S. W. Bailey, C. J. Lambert, S. Sanvito, and J. Ferrer, *Phys. Rev. B* **72**, 045437 (2005).
- ²²A. Ayuela, M. J. Puska, R. M. Nieminen, and J. A. Alonso, *Phys. Rev. B* **72**, 161403 (2005).
- ²³T. Nautiyal, T. H. Rho, and K. S. Kim, *Phys. Rev. B* **69**, 193404 (2004).
- ²⁴M. Wierzbowska, A. Delin, and E. Tosatti, *Phys. Rev. B* **72**, 035439 (2005).
- ²⁵A. Delin and E. Tosatti, *Phys. Rev. B* **68**, 144434 (2003).
- ²⁶J. Fernández-Rossier, D. Jacob, C. Untiedt, and J. J. Palacios, *Phys. Rev. B* **72**, 224418 (2005).
- ²⁷K. M. Smelova, D. I. Bazhanov, V. S. Stepanyuk, W. Hergert, A. M. Saletsky, and P. Bruno, *Phys. Rev. B* **77**, 033408 (2008).
- ²⁸A. Delin, E. Tosatti, and R. Weht, *Phys. Rev. Lett.* **92**, 057201 (2004).
- ²⁹A. Delin and E. Tosatti, *J. Phys. Condens. Matter* **16**, 8061 (2004).
- ³⁰V. S. Stepanyuk, P. Bruno, A. L. Klavsyuk, A. N. Baranov, W. Hergert, A. M. Saletsky, and I. Mertig, *Phys. Rev. B* **69**, 033302 (2004).
- ³¹V. S. Stepanyuk, A. L. Klavsyuk, W. Hergert, A. M. Saletsky, P. Bruno, and I. Mertig, *Phys. Rev. B* **70**, 195420 (2004).
- ³²R. Z. Huang, V. S. Stepanyuk, A. L. Klavsyuk, W. Hergert, P. Bruno, and J. Kirschner, *Phys. Rev. B* **73**, 153404 (2006).
- ³³S. R. Bahn and K. W. Jacobsen, *Phys. Rev. Lett.* **87**, 266101 (2001).
- ³⁴J. L. Costa-Krämer, N. García, P. García-Mochales, M. I. Marqués, and P. A. Serena, in *Proceedings of the NATO Advanced Research Workshop, Miraflores de la Sierra, Madrid, Spain, September 23-27, 1996*, NATO Series E: Applied Sciences, Vol. 340, edited by P. Serena and N. García (Springer, Dordrecht, 1997), pp. 171–190.
- ³⁵Y. Morigaki, H. Nakanishi, H. Kasai, and A. Okiji, *J. Appl. Phys.* **88**, 2682 (2000).
- ³⁶N. Zabala, M. J. Puska, and R. M. Nieminen, *Phys. Rev. Lett.* **80**, 3336 (1998).
- ³⁷B. Sampedro, P. Crespo, A. Hernando, R. Litrán, J. C. Sánchez López, C. López Cartes, A. Fernandez, J. Ramírez, J. González Calbet, and M. Vallet, *Phys. Rev. Lett.* **91**, 237203 (2003).
- ³⁸T. Shinohara, T. Sato, and T. Taniyama, *Phys. Rev. Lett.* **91**, 197201 (2003).
- ³⁹R. Litrán, B. Sampedro, T. C. Rojas, M. Multigner, J. C. Sánchez-López, P. Crespo, C. López-Cartes, M. A. García, A. Hernando, and A. Fernández, *Phys. Rev. B* **73**, 054404 (2006).
- ⁴⁰A. Hernando, B. Sampedro, M. A. Garcia, P. Marin, G. Rivero, P. Crespo, and J. M. Gonzalez, e-print arXiv:cond-mat/0605496.
- ⁴¹Y. N. Kim, E. K. Lee, Y. B. Lee, H. Shim, N. H. Hur, and W. S. Kim, *J. Am. Chem. Soc.* **126**, 8672 (2004).
- ⁴²F. Aguilera-Granja, J. Ferrer, and A. Vega, *Phys. Rev. B* **74**, 174416 (2006).
- ⁴³A. Delin, E. Tosatti, and R. Weht, *Phys. Rev. Lett.* **96**, 079702 (2006).
- ⁴⁴S. S. Alexandre, M. Mattesini, J. M. Soler, and F. Yndurain, *Phys. Rev. Lett.* **96**, 079701 (2006).
- ⁴⁵K. Tsysar, D. Bazhanov, A. Saletsky, V. Stepanyuk, and W. Hergert, *Phys. Solid State* **52**, 641 (2010).
- ⁴⁶P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ⁴⁷G. Kresse and J. Hafner, *Phys. Rev. B* **48**, 13115 (1993).
- ⁴⁸G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ⁴⁹G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ⁵⁰J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ⁵¹P. E. Blöchl, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).
- ⁵²H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ⁵³The distance is defined as an equivalent interatomic distance in a linear chain consisting of the same number of Pd atoms. The actual interatomic distances between the atoms in relaxed configurations are given in the text as necessary.
- ⁵⁴D. Spišák and J. Hafner, *Phys. Rev. B* **67**, 214416 (2003).
- ⁵⁵The system can thus be considered in a twofold view: as being a single atom suspended between two sharp tips or as a 3-atomic chain suspended between quasiflat leads.
- ⁵⁶S. Csonka, A. Halbritter, G. Mihály, O. I. Shklyarevskii, S. Speller, and H. van Kempen, *Phys. Rev. Lett.* **93**, 016802 (2004).
- ⁵⁷M. Kiguchi, K. Hashimoto, Y. Ono, T. Taketsugu, and K. Murakoshi, *Phys. Rev. B* **81**, 195401 (2010).
- ⁵⁸J. Ludwig, D. G. Vlachos, A. C. T. van Duin, and W. A. Goddard, *J. Phys. Chem. B* **110**, 4274 (2006).
- ⁵⁹P. Gambardella, Ž. Šljivančanin, B. Hammer, M. Blanc, K. Kuhnke, and K. Kern, *Phys. Rev. Lett.* **87**, 056103 (2001).
- ⁶⁰K. R. McCrea, J. S. Parker, and G. A. Somorjai, *J. Phys. Chem. B* **106**, 10854 (2002).