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We present a theoretical study of the conductance of atomic junctions comprising single noble gas atoms (He, Ne, Ar, Kr, and Xe) coupled to gold electrodes. The aim is to elucidate how the presence of noble gas atoms affects the electronic transport through metallic atomic-size contacts. Our analysis, based on density functional theory and including van der Waals interactions, shows that for the lightest elements (He and Ne) no significant current flows through the noble gas atoms and their effect is to reduce the conductance of the junctions by screening the interaction between the gold electrodes. This explains the observations reported in metallic atomic-size contacts with adsorbed He atoms. Conversely, the heaviest atoms (Kr and Xe) increase the conductance because of the additional current path provided by their valence p states.

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Noble gases are commonly employed in scanning probe experiments as exchange gases since they are expected to interact weakly with the studied systems. Furthermore, it is often assumed that the adsorption of noble gas (NG) atoms does not affect the electron tunneling between metallic electrodes. However, it has been shown that this is not entirely true. For instance, two decades ago Eigler and coworkers presented scanning tunneling microscope (STM) images of Xe atoms on a Ni(110) surface¹ and they nicely demonstrated that these atoms can be moved to chosen positions on the surface. It has also been shown that it is possible to manipulate individual Xe atoms to construct atomic wires and to measure their electrical resistance² or to functionalize molecules.³

From the theoretical side, while there are numerous works analyzing the interaction between NG atoms and metal surfaces, studies exploring the transport through metal-NG-metal junctions are rather scarce, and most of them have focused either on understanding atomic manipulation or on STM imaging.^{2,4-8} There are still important open problems concerning how adsorbed NG atoms modify the transport through metallic atomic-size junctions. A striking example is the observation made in several break-junction and STM experiments that adsorbed He atoms can strongly modify the current through metallic junctions, lowering in particular the low-bias conductance.⁹⁻¹² This conductance suppression is surprising since the height of the tunneling barrier in the presence of NG atoms has been predicted to decrease;⁵ indeed, Kelvin probe experiments have shown that the work function of noble metal surfaces decreases upon adsorption of Ar, Kr, and Xe.¹³ A possible explanation, based on predictions by Lang,⁴ suggests that adsorbed He atoms can polarize metal states away from the Fermi energy, leading to a decrease in the metal local density of states. This explanation was based on calculations in which the metal electrodes were described by a jellium model (with no atomistic details) and without taking into account van der Waals interactions. Thus, it is highly desirable to revisit this problem with *ab initio* transport methods.

To shed new light on the influence of adsorbed NG atoms in the transport through metallic atomic contacts, we present in this Brief Report a systematic *ab initio* study of the conductance of gold atomic junctions containing single atoms of He, Ne, Ar, Kr, and Xe. Our calculations, based on density functional theory (DFT), show that, while for He and Ne the current flows directly from one metallic electrode to the other, for Ar, Kr, and Xe the transport occurs mainly through the valence p states of the NG atom. In all cases, the presence of NG atoms induces a dipole moment which screens the interaction between the leads. In the case of He, Ne, and Ar the weakening of the metal-metal coupling (rather than a suppression of the metal density of states, as proposed by Lang⁴) leads to a reduction of the tunneling current. On the contrary, for Kr and Xe the additional tunneling path provided by the valence p states overcomes the screening, leading to an enhancement of the current.

Our main goal is to analyze the electronic transport through metallic atomic-size contacts containing single atoms of noble gases. In particular, we have chosen gold for the electrode material and studied the elements He, Ne, Ar, Kr, and Xe. For this purpose, we have carried out conductance calculations within the framework of DFT following the method described in Ref. 14, which is built upon the TURBOMOLE 6.1 code.¹⁵ In all our calculations we have used the BP86 functional.¹⁶ The first step in our analysis is the construction of the atomic junctions. This is done by optimizing geometries where the gold electrodes are formed by two finite clusters of 20 atoms and a single NG atom is placed in the middle. In the optimization, the NG atom and the four innermost gold atoms on each side were relaxed, while the other gold atoms were kept frozen. For the optimized atoms, a def2-TZVP basis set¹⁷ was chosen, while a def-SVP basis set¹⁸ was used for the frozen gold atoms. The binding energies calculated in this way were found to differ by only around 5×10^{-4} eV from those calculated with a def2-TZVP basis set for all the atoms. Subsequently, the gold cluster size was extended to 116 atoms on each side in order to correctly describe the metal-NG atom charge transfer

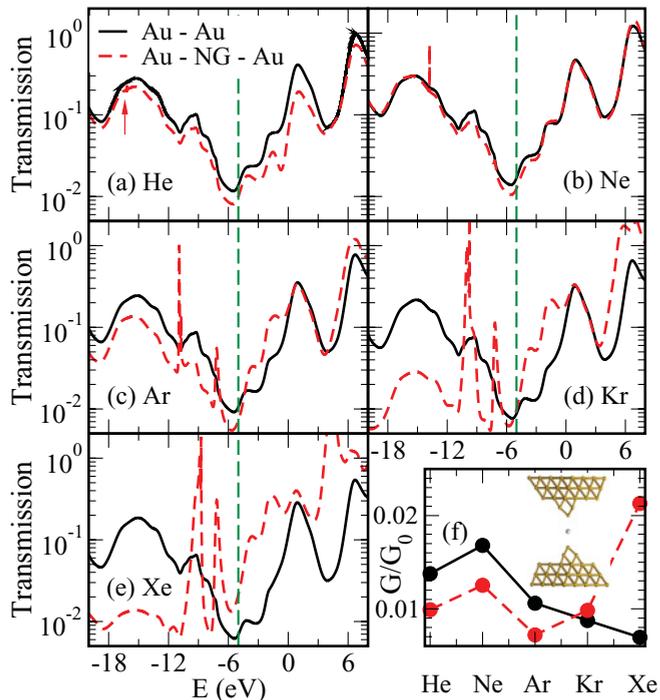


FIG. 1. (Color online) (a)–(e) Zero-bias total transmission as a function of energy for Au-Au (solid black) and Au-NG-Au (dashed red) junctions in the top binding geometry, as shown in the inset of panel (f). The vertical dashed lines indicate the gold Fermi level (-5 eV). (f) Comparison of conductances for Au-Au and Au-NG-Au junctions for all studied NG atoms.

and the energy level alignment [see inset in Fig. 1(f)]. It is important to emphasize that we have used the semiempirical DFT-D2 correction¹⁹ in order to take the dispersive forces into account, since the binding distance between NGs and noble metals is known to be determined by the interplay between the Pauli repulsion and the van der Waals interaction.^{20,21} Finally, the information about the electronic structure of the junctions obtained with DFT is transformed into linear conductance using Green's function techniques as described in detail in Ref. 14. This is done in the spirit of the Landauer approach, where the low-temperature linear conductance is given by $G = G_0 T(E_F) = G_0 \sum_i \tau_i(E_F)$, where $G_0 = 2e^2/h$ is the quantum of conductance, $T(E_F)$ is the total transmission of the junction at the Fermi energy E_F , and $\{\tau_i\}$ are the transmission coefficients, i.e., the eigenvalues of the transmission matrix.

We now start our analysis of the results by comparing the linear conductance of gold junctions containing the five NG atoms considered in this work. We consider first junctions with a top binding position [see inset in Fig. 1(f)], since such a geometry has been suggested as the most favorable for most of the NG atoms on metal surfaces.^{20,22–25} The Au-NG-atom distances and the corresponding binding energies are listed in Table I. In particular, the binding energies increase as we move to heavier elements, in agreement with the calculations of Pershina *et al.*²⁰ In Figs. 1(a)–1(e) we show the zero-bias transmission as a function of energy for the five Au-NG-Au junctions with top binding geometries (dashed lines). Notice that below E_F (marked by a vertical dashed line), pronounced peaks appear, which move toward the Fermi energy as the

TABLE I. Energies of the highest occupied (ϵ_h) and lowest unoccupied (ϵ_l) states for the NG atoms in the gas phase, plus the calculated quantities for the top-binding geometries with a single gold cluster of 116 atoms: binding distance, dipole moment, charge on the NG atom, and binding energy. The value of the dipole in the bare Au cluster is 1.10 debye. Concerning the corresponding quantities in the junction, the binding distances do not change, while the charges on the NG atom and the binding energies are approximately doubled.

Atom	ϵ_h (eV)	ϵ_l (eV)	Au-NG distance (Å)	Dipole moment (debye)	Charges on NG atom (e)	Binding energy (eV)
He	-15.79	16.69	3.41	1.26	0.019	-0.01
Ne	-13.29	14.99	3.28	1.38	0.018	-0.05
Ar	-10.30	10.20	3.55	1.66	0.033	-0.09
Kr	-9.36	6.81	3.63	1.76	0.028	-0.13
Xe	-8.32	4.69	3.73	2.11	0.028	-0.18

atomic number of the NG atom increases. These peaks appear approximately at the energies of the highest occupied states of the NG atoms in the gas phase (see Table I), which suggests that they originate from the valence p states for Ne, Ar, Kr, and Xe, and from the $1s$ state for He. A closer look at the peaks for Ne, Ar, Kr, and Xe shows that they are split into two. One corresponds to the p_z orbital (z being the direction of the junction axis), which is shifted to lower energies, and the second is due to the p_x and p_y states, which remain degenerate in the junction.²⁶ The peak or resonance due to the p_z orbital is clearly broader due to its stronger hybridization with the gold states. Moreover, the width of this resonance increases from Ne to Xe simply because it is determined by the local density of states (LDOS) of the gold tip atoms at the energy of the valence states of the NG atoms. For Ne and Ar, that energy lies outside the $5d$ band of gold, while for Kr and Xe, it is well inside this band. Regarding the conductance, displayed in Fig. 1(f), it varies in a nonmonotonic manner from $10^{-2}G_0$ for He to approximately $2.1 \times 10^{-2}G_0$ for Xe. Notice that the computed conductance for Xe is lower by one order of magnitude than that measured in Ref. 2. We attribute this to the different electrode material (Au rather than Ni).

To understand the mechanism governing the conduction through the NG atoms and how they modify the transport through the gold junctions, we also present in Figs. 1(a)–1(e) the transmission curves for Au-Au junctions (with no NG atoms) and in Fig. 1(f) the corresponding conductance. In these calculations we have kept the gold electrodes at the same distance as in the corresponding Au-NG-Au junctions. The first thing to notice is that for the lightest elements the conductance is lowered when the NG atoms are in the junctions. As explained in the Introduction, such a reduction of the conductance caused by the adsorption of He has been observed in several low-temperature break-junction and STM experiments.^{9,10,12} A similar behavior has been observed for closed-shell molecules such as H_2 .³² For He and Ne, we find that the conductance is decreased by about 30% when these atoms are present. On the contrary, the presence of Kr and Xe in the junctions gives rise to an increase of the conductance, which is larger than a factor of 2 for Xe. What is the reason for

this different behavior? A first hint is obtained by comparing the transmission curves of the junctions with and without NG atoms. As one can see in Figs. 1(a) and 1(b), for He and Ne the transmission curves for the Au-NG-Au junctions follow very closely the energy dependence of the Au-Au junctions. This fact suggests that for He and Ne, the main contribution to the current in the Au-NG-Au junctions comes from direct tunneling from gold to gold, and the only effect of these NG atoms is to reduce the transmission of the gold-to-gold current path. On the other hand, for Ar, Kr, and Xe, the transmission curves differ markedly from those of the Au-Au junctions, especially close to the Fermi energy. This suggests that the valence p states of these atoms are contributing significantly to the transport through these junctions.

The fact that He and Ne do not contribute to the electronic transport is reasonable, as their highest occupied states lie very far away from the Fermi level and they are weakly coupled to the electrodes. The conductance suppression is, however, surprising, as it is, *a priori*, not obvious how a closed-shell atom can conduct less than the vacuum. We explain this suppression as follows. In our analysis of the interaction between a NG atom and a single gold cluster we have found that there is a tiny charge transfer (a fraction of an electron leaves the NG atoms), which induces a dipole moment pointing away from the metal.²⁷ The values of the charge transfers and the dipole moments are reported in Table I. The existence of this dipole moment has been predicted by numerous authors in the context of NG atoms adsorbed on metal surfaces.^{6,20,25,28–30} Also in that context, it has been argued that as a consequence of the induced dipole the charge is pushed from the interstitial vacuum region toward the Au bulk (the so-called pillow or cushion effect). In our case, we did not find a notable charge depletion on the gold tips. We also did not find any significant change in the LDOS of the gold tips at the Fermi level, as was proposed by Lang⁴ (see Ref. 26) or more recently by Weiss *et al.*³² for the H₂ case. Therefore, we suggest that, at least for He and Ne, what causes the current suppression is the induced polarization which decreases the coupling between the two leads, reducing the transmission of the direct gold-to-gold path. The discrepancy between our results and those of Ref. 4 could be due to the limitations of the jellium model used in that work.

Convincing evidence of the validity of our arguments above is provided by the analysis of the conduction channels. In the left panels of Fig. 2 we show both the total transmission and the individual transmission coefficients $\{\tau_i\}$ as a function of energy for the Au-Au, Au-He-Au, and Au-Xe-Au junctions. In the Au-Au junction the interelectrode distance is the same as in the Au-He-Au junction. In all cases, the transmission at the Fermi energy is dominated by a single channel. More importantly, the transmission coefficients are very similar for the Au-Au and the Au-He-Au junctions, suggesting a common transport mechanism, whereas for the Au-Xe-Au junction new features are visible around E_F , originating from valence p states of the Xe atom. The nature of the dominant channel at E_F can be established by looking at the corresponding wave functions of this eigenchannel. Such (right-moving) wave functions for these three junctions are shown in the right panels of Fig. 2. They have been calculated using the method described in Ref. 31. Notice that there is no weight present in the gap

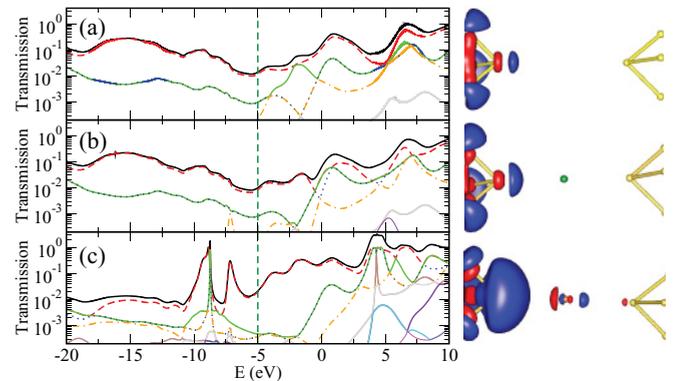


FIG. 2. (Color online) The left panels show the total transmission (solid lines) and the largest transmission coefficients (dashed lines) as a function of energy for (a) Au-Au, (b) Au-He-Au, and (c) Au-Xe-Au junctions. The transmission coefficients have been classified according to the magnitude of the eigenvalue. The right panels show the corresponding right-moving wave functions of the dominant eigenchannel at the Fermi energy for the same isosurface values.

region either in the Au-Au junctions, as expected, or in the Au-He-Au one. On the other hand, in the Au-Xe-Au junction the channel in the central region has the symmetry of the Xe p_z orbital, demonstrating that this orbital plays the main role in the conduction through this junction, as hinted in Ref. 33. This is at variance with the calculations of Ref. 7, where the transport through Xe was found to occur through the tail of the $6s$ orbital.

We have checked that the qualitative behavior of the different NG atoms is also exhibited in other binding geometries. An example of Au-He-Au and Au-Xe-Au junctions with hollow binding geometries is shown in Ref. 26. On the other hand, one may wonder whether the special behavior of the He is sensitive to the interelectrode distance. This is an important question since experimentally it is not easy to determine absolute distances, and the influence of the He atoms has been deduced from the conductance decay when the junctions are stretched toward the tunnel regime. To answer this question, we have simulated the stretching of a Au-He-Au junction starting from the equilibrium geometry of Fig. 1. For these calculations we have modeled the narrowest part

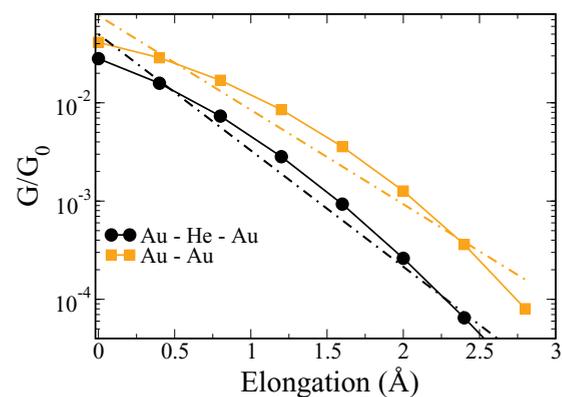


FIG. 3. (Color online) Conductance vs elongation for Au-Au and Au-He-Au junctions upon stretching (solid lines) and fitting curves to an exponential function (dashed-dotted lines), see text.

of the electrodes with clusters of 20 gold atoms, and have checked that the results are consistent with those obtained with the larger clusters. In Fig. 3 we show the evolution of the conductance of the Au-He-Au junction upon separating the gold electrodes symmetrically from the He atom in the equilibrium position. For comparison we also include the results for the corresponding Au-Au junction. Figure 3 shows that the presence of the He atom suppresses the conductance also at larger distances. The conductance decay for both junctions can be roughly fitted with an exponential function $G = A e^{-\beta d}$, where β is the attenuation factor and d corresponds to the elongation, as measured with respect to the equilibrium position. The attenuation factor β is equal to 2.72 \AA^{-1} for the junction with the He atom and 2.21 \AA^{-1} for the pure gold junction. The faster decay with the He atom is consistent with the experiments,^{9,10,12} and it shows that the conductance suppression can be more dramatic at large distances (up to 82%).

In summary, we have presented a theoretical analysis of the influence of NG atoms on the conductance of gold atomic

contacts. We have shown that He and Ne atoms do not conduct and their effect is to reduce the conductance of the metallic junctions due to polarization effects. As we consider the tunneling current through heavier noble gas atoms, the polarization effects increase but they are compensated for by an increasing contribution of the valence p states of the NG atoms, leading to an enhancement of the conductance. Our study shows that the presence of adsorbed NG atoms can modify significantly the conduction through atomic-scale junctions, which has important implications for a great variety of experiments in the field of molecular electronics.

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