

Structure and quantum effects in atomic-sized contacts

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Ab initio studies reveal the interplay between structure and quantum effects in atomic-sized Cu nanocontacts. Our approach is based on density functional theory within the frame of a Korringa-Kohn-Rostoker Green's function method. We present evidence that the electronic structure of nanocontacts during stretching is governed by quantum-mechanical resonances. Our results indicate that the quantum size-effects have a profound effect on electronic states of contacts before breaking.

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The rapid miniaturization of electronics to the nanometer scale is a key force driving intensive investigations of mechanical, electrical, and magnetic properties of atomic-sized metallic contacts.¹ Nanocontacts have been fabricated using the scanning tunneling microscope (STM)² and break-junction techniques.³ If the size of such structures approaches an atomic dimension, quantum-mechanical effects prevail and cause interesting new behavior. In this way, for example, anomalous dependence of resistance on length in atomic wires has been found,⁴ spontaneous magnetization of simple metal nanowires has been predicted⁵ and the Kondo effect has been observed⁶ in quantum point contacts. Recent experiments have shown that it is possible to shrink the contact to just a few atoms, or even to its minimal possible size, a single atom.^{2,3,7}

One of the central issues in physics of nanocontacts is the interplay between atomic structure and electronic states. Theoretical studies have predicted that mechanical and transport properties of nanocontacts are strongly affected by their detailed local atomic arrangement. Different semiempirical potentials⁸⁻¹⁰ and the effective-medium theory^{11,12} have been used to determine the structure of the contacts. For example, performing molecular dynamics simulations for Au nanocontacts, Landman *et al.*⁸ showed that the elongation of the contact proceeds through successive stress accumulation and relief stages. The calculations of the conductance of metallic contacts in the tight-binding approximation revealed that abrupt structural changes lead to abrupt changes in the conductance.⁹ The correlation between the structure of gold nanowires and the conductance has been found in recent experiments.^{13,14}

Although the above mentioned theoretical methods provides an appealing picture of the formation mechanism of nanocontacts, they become less effective for a quantitative description of bonds in low-coordinated system, such as one-dimensional contacts. Several *ab initio* studies of atomic contacts have been performed, mainly within the jellium model.^{1,15} There is clearly need for *ab initio* studies of electronic properties of nanocontacts which can take into account the structure of contacts and electrodes. Such calculations are much more demanding when d electrons are important.

The goal of this Brief Report is to present the *ab initio* Korringa-Kohn-Rostoker (KKR) Green's function method

for studies of structural and electronic properties of nanocontacts. As an example, we discuss the Cu atomic-sized contacts. The interplay between structure and quantum states of contacts is demonstrated. We reveal that the electronic structure of contacts before the breaking point is dominated by quantum size effects.

Our self-consistent calculations are based on the density functional theory in the local density approximation (LDA) within a KKR Green's function method.¹⁶ We apply multiple-scattering theory to describe the scattering of electrons by effective one-electron potentials of the contact and electrodes. First, we treat an electrode as a two-dimensional (2D) perturbation of the bulk. By removing the atomic potentials of a few crystal layers we create two electrodes being practically uncoupled. The ideal crystal is considered as the reference system for the calculation of the ideal electrodes. Taking into account the 2D planar periodicity of electrodes we solve a Dyson equation for the structural Green's function of the electrode.¹⁶ We allow the potentials of a few subsurface layers (typically 3–4) to be perturbed. Using a multipole expansion the full charge density is taken into account. Our test calculations showed that only the spherically symmetric part of the potentials inside Wigner-Seitz spheres is important for calculations of electronic states, magnetic properties and total energies of atomic contacts. However, we use the full-potential KKR Green's function to determine the Hellmann-Feynman forces acting on atoms near electrodes.¹⁷

The atomic contact suspended between the two electrodes destroys the 2D periodicity. The structural Green's function of the ideal electrodes is then used as the reference Green's function for calculations of the Green's function of the atomic contact.

The potentials of all atoms of the contact, vacuum sites adjacent to the contact and reference sites of electrodes are considered to be perturbed, i.e., they are treated fully self-consistently. For example, for the calculation of electronic states of atomic chains of 5–7 atoms suspended between the two infinite electrodes we have to calculate self-consistently about 50–70 atoms. Recent development of the screened KKR Green's function method has made it possible to calculate fully self-consistently atomic contacts of several hundreds atoms.¹⁸ In comparison to jellium models, our method

takes into account the atomic structure of the contact and electrodes. Both nonmagnetic and magnetic systems can be calculated on the same footing.

Several experiments and calculations have given direct evidence that bonds of low coordinated metal atoms are considerably stronger than bonds in the bulk.^{11,13} Therefore, to determine the equilibrium atomic structure of the contacts and electrodes we construct interatomic potentials by fitting the parameters of interactions simultaneously to the first principle surface and bulk calculations. Potentials are formulated in the second moment tight-binding approximation.¹⁹ Binding energies of supported clusters of different sizes and geometries, Hellmann-Feynman forces acting on atoms near electrodes and surface energy are accurately fitted to correctly describe interactions between atoms for low-dimensional systems. To link the interaction between atoms near the surface to that in the bulk the set of data used for fitting includes such bulk properties as bulk modulus, lattice constant, cohesive energy, and elastic constants calculated in the LDA approximation.^{20,21} This method can also be used for binary systems where the parameters of cross interactions are determined in the same manner.²² The combination of *ab initio* and TB methods allows one to construct many-body potentials for low-dimensional structures and to perform atomic relaxations for very large systems having d electrons, which are still out of possibilities of *ab initio* methods. We use these potentials for structural optimization of nanocontacts and apply the *ab initio* KKR Green's function method for self-consistent calculations of electronic states in the fully relaxed geometry

We first discuss stress variation during the stretch of the nanocontacts. Stress calculations are performed using many body potentials described above. As an example, our results for the Cu chain of five atoms suspended between Cu electrodes are presented.²³ We perform calculations of the atomic level stress components²⁴ $\sigma_{\alpha\beta}(i) = -1/\Omega_0 [p_i^\alpha p_i^\beta / m_i + \frac{1}{4} \sum_j (r_{ij}^\beta f_{ij}^\alpha + r_{ij}^\alpha f_{ij}^\beta)]$, with $(\alpha, \beta) \equiv (x, y, z)$, m_i and p_i are the mass and momentum of atom i , \vec{r}_{ij} means the distance between atom i and j , and \vec{f}_{ij} is the force acting on atom i due to j , Ω_0 defines the average atomic volume. We perform calculations at $T=0$ K, therefore the momenta are equal zero. The atomic level stress can be regarded as the local response of the system to the virtual strain and can be used as a physically appropriate description of its local structure.²⁴

Figure 1 shows the average hydrostatic stress $P_\sigma = \text{Tr}(\sigma_{\alpha\beta})$ in the Cu chain for fixed number of atoms but increasing distance between the electrodes. During the initial stages of stretching the chain is under strong compressive stresses (point a in Fig. 1). The compressive stress in the chain decreases linearly with increasing distance between electrodes (point b in Fig. 1). Beyond a certain distance, the tensile stress develops and upon further stretching the tensile stress decreases abruptly (point c in Fig. 1) and the contact finally breaks.²⁵

We find that the atomic resolved stress in the compressed Cu chains is strongly inhomogeneous (see Fig. 1, inset), while it becomes homogeneous upon further stretching. The deformation of the electrodes is shown in Fig. 2. One can see

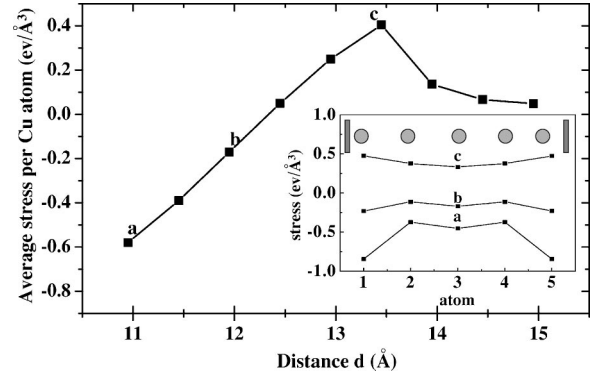


FIG. 1. Averaged hydrostatic stress P_σ in the Cu contacts; inset: atomic resolved stress. The transition from the compressive stress (a and b points) to the tensile one (c point) is seen.

that the electrodes in a fully relaxed geometry are not flat anymore. The atoms of the electrodes in the area of the contact are strongly pushed inward if the contact is under compressive stress. During stretching of the contact the atoms of the electrodes are pushed up and before the breaking point strong outward atomic displacements are found.

In order to get insight into the interplay between the structure of contacts during the breaking process and their electronic states we calculate the local density of states (LDOS) corresponding to the compressive stresses (a and b points in Fig. 1) and the tensile stress (c point in Fig. 1). In Fig. 3 the s components of LDOS are shown for all atoms of the contact for different distances between electrodes.

The calculated LDOS can be compared with the idealized 1D behavior, which is characterized by a sharp peaks and a $E^{-1/2}$ decay with increasing energy. A broadening of the resonances in the LDOS is attributed to the finite length of the contact and the interaction with electrodes. One very fundamental issue demonstrated by these results is the strong impact of the structure of the contact on its electronic states. In particular, one can see that during the breaking process resonances in the LDOS move to lower energies and unoccupied electronic states approach the Fermi level. These results reflect qualitatively the L^{-2} (L is the distance between

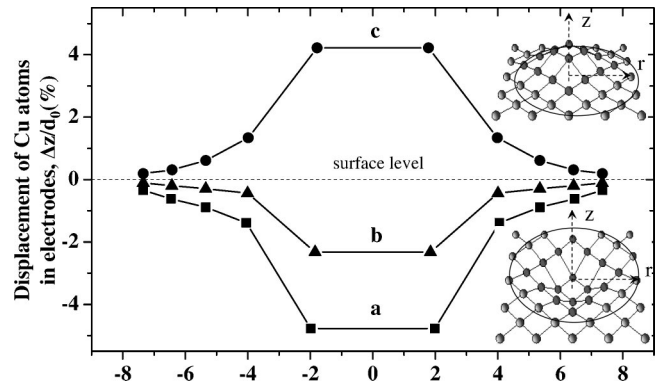


FIG. 2. Atomic displacements in the electrodes relative to the surface for the compressive (a and b points) and for the tensile stages (point c) during stretching of the contact, $d_0 = 1.8075$ Å; the fcc (001) surface is considered for electrodes.

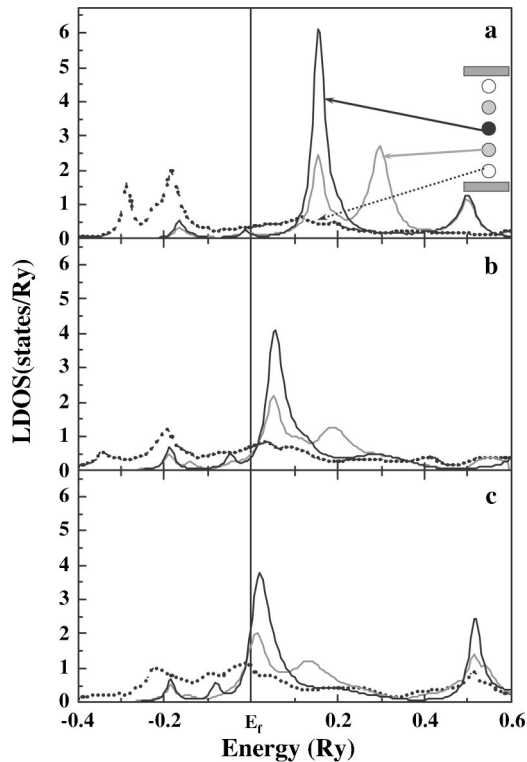


FIG. 3. Atomic resolved s -LDOS in the Cu contact consisting of 5 atoms for different distances between electrodes.

electrodes) dependence of peak positions of the 1D particle in the quantum box model. While this model is certainly oversimplified for our case, it explains that for increasing length of the contact resonances are shifted to lower energies.

Our calculations reveal that shortly before the breaking unoccupied resonances cross the Fermi level (see Fig. 3). As the result of this effect, the LDOS at the Fermi level and the charge density of s -electrons are strongly enhanced.²⁶ These findings indicate the interplay between mechanical and quantum properties of the Cu contacts during the stretch.

For our discussion, we recall the recent analysis of Stafford *et al.*,²⁷ who considered the quantization of the electronic motion in the contact within jellium model and found the correlation between the cohesive and electronic properties. The contact between two pieces of metal can be thought of as a waveguide for conduction electrons. The atomic contact confines electrons to propagate only in one dimension. The interatomic distances in the contact are of the order of the wavelength of the electrons, therefore the quantum-mechanical wave nature of the electrons should be important. Emberly and Kirczenow have shown that electron transport through atomic contacts can be explained in terms of electronic standing waves.²⁸ These waves are formed along the

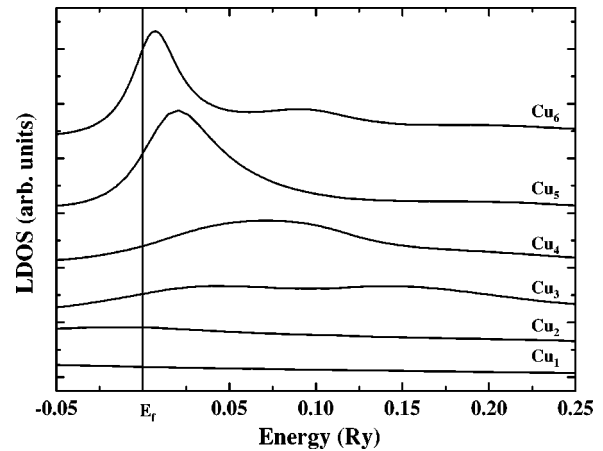


FIG. 4. The quantum size effect: development of 1D electronic structure in the Cu contacts before breaking; s -LDOS are presented.

contact due to the interference of electronic waves scattered from the two electrodes. While the contribution of quantum modes to structural properties of atomic contacts is still under debate,¹ our results provide the strong evidence for the correlation between quantum effects and mechanical properties on the atomic scale. An enhancement of the LDOS at the Fermi level shortly before the breaking may influence the transport properties through atomic contacts drastically. For example, it was found that the conductance of the Al neck increases shortly before the breaking.²⁹

Finally, we demonstrate that quantum size effects in the electronic properties of single-atomic contacts and mono-atomic chains are important. We considered 1D Cu chains consisting of 1 to 6 atoms. For every chain before breaking the equilibrium positions of the atoms in the chain and in the electrodes have been determined. Afterwards a self-consistent calculations of the LDOS are performed for all chains in a fully relaxed geometry. The calculated LDOS in the middle of the chains are presented in Fig. 4. Our results show dramatic changes in the electronic properties of contacts as the number of atoms increases. Gradual development of 1D electronic states is well seen. The size effect is found to be dominated by unoccupied electronic states and leads to an enhancement of the LDOS at the Fermi level as the number of atoms in the contact increases.

In summary, the *ab initio* studies have shown that structure, electronic and mechanical properties of the one-dimensional contacts are strongly related. We have demonstrated that electronic states in the contacts before breaking are drastically influenced by quantum size effects. We believe that our results are of fundamental importance for understanding and control of the size-dependent electronic properties of nanocontacts.

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