

Extraordinary Electron Propagation Length in a Metallic Double Chain Supported on a Metal Surface

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The present theoretical study shows that a double chain of Cu metal atoms adsorbed on a Cu(111) metal surface can guide an excited electron for distances exceeding 10 nm. The nanostructure appears to be quasi-decoupled from the substrate and thus to act as a nanowire. The origin of the above phenomenon is the interference between the decay of the quasistationary 1D sp -band states localized on each chain. This allows to approach the situation of the formation of bound states in the continuum first discussed in quantum systems by von Neumann and Wigner.

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Miniaturization of electronic devices down to the scale where quantum-mechanical effects become important, prompted an intense research in nano- and molecular electronics [1]. The effort is often focussed on finding nanoanalogs to existing macro devices so that one would be able to construct nanoelectronic circuits with the same operative properties as macro electronic ones [2]. Among various components of nanoelectronic devices, the nanowires insulated from the surrounding and connecting metal leads have been thoroughly studied over the past years, and a deep understanding of the major phenomena controlling the electron transport in such systems has been reached [1,3–6].

In this Letter we show, that a linear metal nanostructure directly deposited on a metal can act as a nanowire. We demonstrate that two infinite parallel monatomic chains of metal atoms supported on a metal surface (Fig. 1) can guide an excited electron over a distance exceeding 10 nm. This structure has no macroscopic analog since insulation in its conventional sense is absent. Instead, the insulation is brought by the quantum-mechanical phenomenon first addressed by von Neumann and Wigner [7], and known as formation of bound states in the continuum [8]. The above result is robust and can be explained within the framework of the theory of interacting resonances [9–11].

Before entering into the specific details of the calculations, let us first discuss some general properties of metal supported monatomic chains. Metal monatomic chains were built recently by scanning tunneling microscope manipulation of Au and Pd atoms on a NiAl(110) surface [12–14], as well as of Cu atoms on Cu(111) [15,16], and Ag atoms on Ag(111) [17]. Despite different (adsorbate)/(substrate) combinations, common features have been revealed by experiments and by *ab initio* theoretical studies [15,17–20]. The monatomic chains support a chain-

localized 1D sp band of excited electronic states located above the Fermi level and in the projected band gap of the substrate. The 1D sp -band states are quasistationary and decay by the energy conserving resonant electron transfer (RET) into the substrate. For example, in the Cu-chain/Cu(111) system, an electron excited into the 1D sp band travels over an average distance of at most 15 Å (5 interatomic spacings) along the chain before escaping [18].

Here, instead of a single chain, we address the excited electron dynamics in a double Cu chain deposited at a Cu(111) surface in the symmetric arrangement shown in Fig. 1. Particular emphasis is put on the emergence of the long-lived “molecular” states resulting from the interaction between the quasistationary 1D sp -band states localized on each chain. The chains are along one of the $\langle 110 \rangle$ directions of the surface with Cu adatoms occupying the fcc adsorption sites spaced by $a/\sqrt{2}$, where $a = 3.59$ Å is the lattice constant of Cu. The distance between the chains is given by $h = jh_0$, where j is an integer and $h_0 = a\sqrt{3}/2 = 8.3a_0$ (atomic units are used unless other-

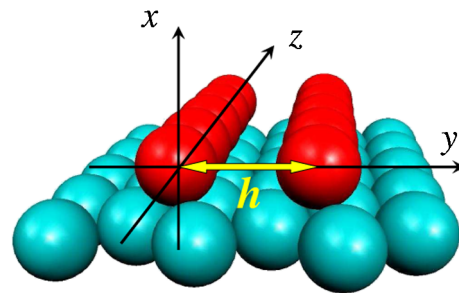


FIG. 1 (color online). Schematic representation of a double Cu chain supported on a Cu(111) surface. The Cu atoms in the chains [red (dark gray)] are adsorbed in fcc sites of the surface and along one of the $\langle 110 \rangle$ directions.

wise stated). The distance between the Cu chains and the last layer of surface atoms is 1.92 Å, as obtained previously [18].

The energies, decay rates, and wave functions of the quasistationary states localized at the nanostructure are obtained with the wave packet propagation (WPP) approach. The method consists in the solution of the time dependent Schrödinger equation for an excited electron. The WPP is detailed in Refs. [18,21], where quantitative account of the experimental data for the single Cu chain on Cu(111) is reached. For the double chain structure, the total potential V “seen” by an excited electron is defined as: $V = V_M + V_{\text{ch}}(x, y, z) + V_{\text{ch}}(x, y - h, z)$. V_M stands for the model electron-Cu(111) surface interaction potential [22]. $V_{\text{ch}}(x, y, z)$ is the change of the electron-surface interaction because of the presence of a single chain. It is obtained on the basis of *ab initio* density functional theory studies performed in the supercell geometry for the clean Cu(111) surface and Cu-chain/Cu(111). The 4×1 surface unit cell (y and z directions, respectively) has been used with a distance between the adjacent Cu chains of $16.6a_0$. The procedure developed and tested in Refs. [18,21] allows extraction of the single chain potential $V_{\text{ch}}(x, y, z)$ free of the periodicity effects due to the supercell. Thus, the construction of the double chain potential as an independent sum of $V_{\text{ch}}(x, y, z)$ potentials is not limited to $h = 16.6a_0$, but is applicable for the whole range of the inter-chain distances h considered here. This is further supported by the analysis of the present density functional theory results.

In Figs. 2 and 3 we show the energies and decay rates of the double chain states for two distances between the chains: $h = 8.3a_0$ and $h = 16.6a_0$. The dispersion curve of the 1D sp band of the single chain is split in two branches. Symmetric and antisymmetric molecular states are formed. The states disperse parabolically reflecting the quasifree electron motion along the structure with an effective mass $m^* \approx 0.5$. For the electron momentum parallel to the structure k_z below 0.4 a.u., the band folding [23] is not effective, and the double chain states are in the projected band gap of the substrate. The projected band gap reduces the efficiency of the RET from the nanostructure into the substrate [24–27]. Indeed, it follows from Fig. 2(a) that the double chain-localized states are in energy resonance with 3D bulk states or with the surface state continuum only at finite values of the electron momentum perpendicular to the wire k_y . Electron transfer close to the surface normal is impossible.

Most importantly, as seen in Fig. 3, the decay rates of the quasistationary symmetric and antisymmetric double chain states are very different from the decay rate of the 1D sp band of the single chain. For $h = 8.3a_0$ the decay rate of the symmetric state is more than 1 order of magnitude smaller than that of the 1D sp -band state of the single chain. At variance, the antisymmetric state decays faster

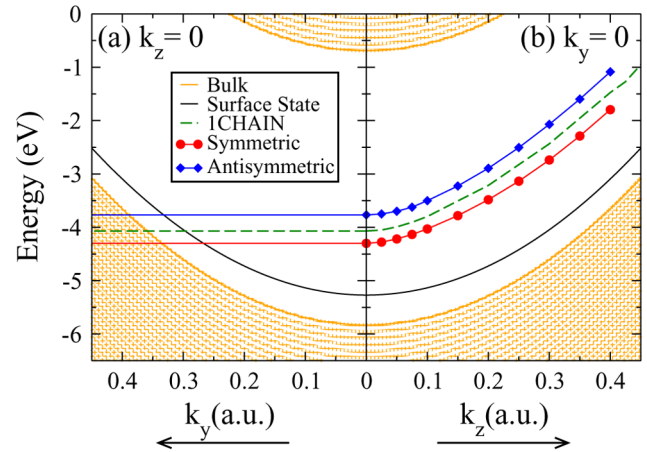


FIG. 2 (color online). Energy dispersion of the quasistationary 1D sp -band states localized on the double chain (lines with symbols) and single chain (dashed line) of Cu atoms on Cu(111). For the double chain structure, the distance between the chains is $h = 8.3a_0$. The surface state (black line) and 3D bulk states of the substrate (hatched area) are also shown. The white area corresponds to the projected band gap of the substrate. The results are presented as a function of the electron momentum perpendicular k_y and parallel k_z to the structure. Panel (a) corresponds to $k_z = 0$. Observe that the 1D sp -band states are localized along the y direction and so do not disperse with k_y . Panel (b) corresponds to $k_y = 0$.

than the single chain state. The situation is inverted for the double distance $h = 16.6a_0$, where the antisymmetric state has a very small decay rate while the symmetric state is destabilized.

Further insight into the decay process and unambiguous symmetry assignment of the double chain-localized states

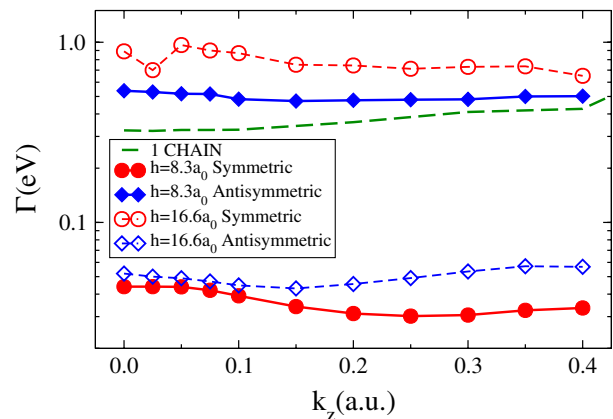


FIG. 3 (color online). RET decay rates of the quasistationary 1D sp -band states localized on the double chain (lines with symbols) and single chain (dashed line) of Cu atoms on Cu(111). The results are presented as a function of the electron momentum k_z along the structure. For the double chain structure the results are presented for two distances between the chains $h = 8.3a_0$ (filled symbols), and $h = 16.6a_0$ (open symbols).

are obtained from their electronic densities presented in Fig. 4. The WPP results clearly show symmetric and antisymmetric combinations of the 1D sp bands localized on each of the chains (for the electronic density of the 1D sp band see Refs. [17–19]). The maximum density is above the chains with both sp hybrids slightly tilted with respect to the surface normal because of the interaction. The decay of the quasistationary states appears as an outgoing electron flux into the bulk (red arrows) and into the surface state continuum in the direction parallel to the surface (white arrows). Observe that the decay into the bulk states reveals a well marked directionality, i.e., an electron is transferred with the smallest possible k_y [see Fig. 2(a)]. The relative intensity of outgoing fluxes shows that decay into the surface state continuum dominates, similar to the single chain case [18]. Consistently, with the decay rates presented in Fig. 3, the small decay rate of a state is associated with a nearly suppressed outgoing electron flux.

The physics behind the above results can be understood from a model perturbative approach describing the coupling between the states localized on each chain and the surface state continuum. Following Ref. [11], the dynamics of an excited electron with a given momentum k_z is governed by an effective non-Hermitian Hamiltonian:

$$H = \begin{pmatrix} E(k_z) - i\Gamma(k_z)/2 & W - i\Gamma(k_z)e^{ik_y h}/2 \\ W - i\Gamma(k_z)e^{ik_y h}/2 & E(k_z) - i\Gamma(k_z)/2 \end{pmatrix}, \quad (1)$$

where $E(k_z)$ and $\Gamma(k_z)$ are the energy and decay rate of the 1D sp -band states of the single chain, and W (real) is a parameter describing the direct chain-chain coupling. The nondiagonal term proportional to $\Gamma(k_z)$ corresponds to the surface state continuum mediated indirect chain-chain coupling between the 1D sp -band resonances. The wave vector k_y of the electron in the surface state continuum is obtained from the energy conservation condition: $E(k_z) =$

$E_0 + (k_y^2 + k_z^2)/2$. $E_0 = -5.3$ eV (with respect to the vacuum level) is the energy of the Shockley surface state at $\bar{\Gamma}$ point [22]. Here we have taken into account that the model potential V_M [22] implies an effective mass equal to one for the surface state.

The quasistationary symmetric (S) and antisymmetric (A) states of the system correspond to the eigenstates of the Hamiltonian given by Eq. (1). Their energies $E_{S/A}$ and decay rates $\Gamma_{S/A}$ are given by:

$$\begin{aligned} E_{S/A}(k_z) &= E(k_z) \pm W \pm \Gamma(k_z) \sin(k_y h)/2, \\ \Gamma_{S/A}(k_z) &= \Gamma(k_z)[1 \pm \cos(k_y h)]. \end{aligned} \quad (2)$$

The decay rates of the symmetric and antisymmetric state appear independent of the direct coupling W , and Γ_S or Γ_A vanish whenever the distance between the chains h is such that $k_y h = n\pi$ with n integer. The double chain-localized excited state becomes decoupled from the substrate. Intuitively, the outgoing fluxes from the resonances localized on each chain appear with a relative phase equal to π and cancel each other at infinity. We stress that the weak coupling between the chains leading to the effective Hamiltonian (1) is an essential condition for the above phenomenon. Close packed arrangements are not expected to support the long-lived state.

For the present system, h is not a continuous parameter. Since the adatoms have to be placed at specific sites at the surface, h changes by multiples of $h_0 = 8.3a_0$. For $0 \leq k_z \leq 0.4$ a.u., we have: $2.52 \leq h_0 k_y \leq 2.91$. Thus, the stabilization condition is nearly fulfilled for the symmetric state for $h = h_0$, and for the antisymmetric state for $h = 2h_0$. This is in full agreement with the present WPP results. It is noteworthy that the above analytical demonstration only considers the coupling to the surface state continuum. It follows from our numerical results that an additional weak coupling to the 3D propagating bulk states does not destroy the present effect. In fact, provided the directionality of the outgoing flux into the 3D bulk states, one can argue that *both* decay rates, into the surface state continuum and into the 3D bulk continuum, should be reduced in the same range of h .

How general is the above phenomenon? The surface supported metallic chains studied so far present an excited 1D sp band of quasistationary electronic states [12–17]. For two identical chains deposited on a surface with a projected band gap, from the general theory of interacting resonances [9,10] one can expect that one of the molecular states issuing from the interaction between the two identical “parent” resonances will have a smaller decay rate than the parent state. The effect can be tuned via a proper choice of the interchain distance h . It is noteworthy that the surface state mediated coupling has been also reported in the context of the scanning tunneling microscope spectroscopy of Kondo atoms [28], and the bound states in the continuum were demonstrated for photonic structures [29].

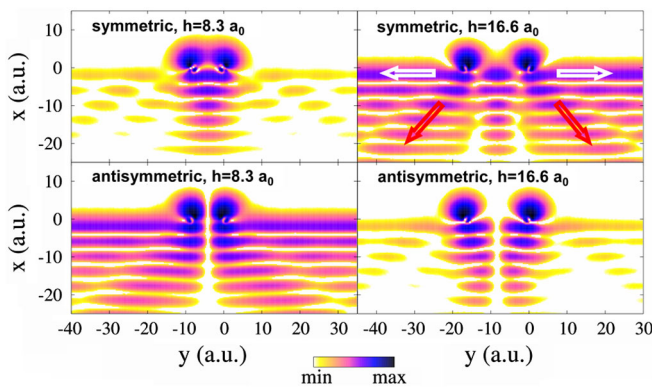


FIG. 4 (color online). Electron density of the quasistationary states localized on a Cu double chain supported on Cu(111). The figure presents the logarithm of the electron density for $k_z = 0$, and for the two interchain distances h given in the insets. Results are shown in the (xy) plane as defined in Fig. 1. Arrows mark the electron flux outgoing into the surface state (white) and 3D bulk (red).

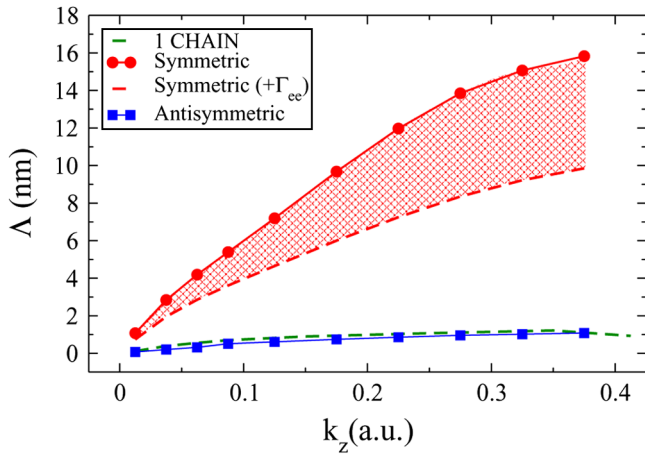


FIG. 5 (color online). The distance traveled by an excited electron along the double chain structure Λ . The distance between the chains $h = 8.3a_0$. Results are shown as a function of the electron momentum k_z . The hatched area gives the range of Λ obtained without (red line with circles) and with (dashed red line) account for the many body decay.

Finally, the average distance Λ traveled by an excited electron along the double chain structure can be obtained as the product of the lifetime and the group velocity:

$$\Lambda_{S/A}(k_z) = [\Gamma_{S/A}(k_z) + \Gamma_{ee}]^{-1} \partial E_{S/A}(k_z) / \partial k_z, \quad (3)$$

Γ_{ee} is the many body contribution to the decay of the nanostructure localized state [26]. Indeed, the rate of the resonant electron transfer into the substrate is so small for one of the molecular states, that many body decay has to be taken into account. The calculation of Γ_{ee} has not been attempted here. Rather, based on reported studies we estimate $\Gamma_{ee} \leq 20$ meV [26].

In Fig. 5 we show $\Lambda(k_z)$ for the distance between the chains $h = 8.3a_0$. The hatched area gives the range of travel distances obtained with and without account for the many body decay of the chain-localized symmetric state. As follows from our results, the symmetric state of the double chain structure appears strongly decoupled from the substrate and, *de facto*, plays the role of an insulated nanowire. An electron excited in this state can propagate along the structure for a distance of the order of 10 nm, i.e., by more than 1 order of magnitude larger than the propagation distance along the single chain reported in Ref. [18]. For $h = 16.6a_0$ a similar result is obtained for the antisymmetric state.

In conclusion, on the example of two parallel Cu chains adsorbed on Cu(111) we have demonstrated that the structure made of two monatomic chains of metal atoms directly deposited on the metal surface can play the role of a nanowire, and guide an excited electron for a distance exceeding 10 nm. The decoupling of the nanowire from the substrate has its origin in the quantum-mechanical

phenomenon known as formation of bound states in the continuum. The effect is general provided the substrate possesses a surface-projected band gap.

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