Local electronic properties in nanoscale systems

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The local electronic structure on nanoscale chains is investigated theoretically. We propose a mechanism to explain the even-odd oscillation of length distribution of atom chains. We study the spatial peak structure as obtained by scanning tunneling microscopy (STM) constant-current topography as a function of the electron-electron interaction, band filling and temperature. The site-dependent magnetic moment is also examined.

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I. INTRODUCTION

The recent development of techniques capable of constructing structures on the nanoscale, with dimensions that are intermediate in size between isolated atoms/molecules and bulk materials, has opened up numerous possibilities for constructing new devices. This perspective raises the importance about novel and improved physical, chemical, mechanical, and biological properties of nanoscale atomic clusters. In particular, a relatively recent focus has been to study the effects of the electronic quantum confinement within finite length chains.\textsuperscript{1,2,3,4,5,6} With the help of scanning tunneling microscopy (STM) the formation of quantized chain-localized states in the pseudogap of the substrate bulk band in chains at semiconductor or insulator surfaces has been observed.\textsuperscript{1,2,3}

The investigation of the electronic properties of nanoscale atomic clusters is particularly interesting. The electronic properties suffer strong effects due to the finite length of chains. The breaking of translational symmetry creates electronic end states. The electronic quantum confinement in finite length segments changes the density of states within the chains. The conductivity along the chain shows spatial variations in the electronic density of states.\textsuperscript{1,2,3} The direct observation of the local electronic structure on a nanoscale atomic chain by STM stresses the importance of exploring these effects theoretically.

We can observe that while some STM measurements can be explained on the basis of non-interacting electrons,\textsuperscript{1,2,3} others instead suggest strong interaction between electrons\textsuperscript{5} indicating the possibility of a description using the Hubbard model. The significance of the results for extremely small systems without a systematic analysis of the observed effects for larger systems would not have been appropriate some years ago, when the investigation of new nanoscale devices was known only as a theoretical possibility. Since the experimental skills to manipulate the nanostructures, this study has become important, not only to obtain new insight regarding properties of theoretical models, but certainly also to better understand physical properties in this class of systems.

In this paper we study theoretically the local behavior of the physical quantities of open chains on the nanoscale. We report on site-dependent properties of the electronic quantum confinement within finite length chains. This theory allows for an interpretation of experimental results on finite-size effects. We studied two different aspects of these systems. First, considering only the electronic structure, we introduce a model that captures qualitatively the experimental chain lengths distribution. For this case, we analyzed the internal structure of atom chains by examining the site-dependent occupation number along the axis of the chain for one electron. Secondly, we studied the electron-electron interaction by using the Hubbard model to understand the main effects of the electronic quantum confinement within finite length chains.

The organization of this paper is as follows. Our investigation of the chain lengths distribution using the tight binding approach is presented in Sec. II. The results for local occupation numbers and for the site-dependent magnetic moment as a function of the electron-electron interaction, band filling and temperature on electronic quantum confinement within finite length chains are presented in Sec. III. Our conclusions are presented in Sec. IV.

II. TIGHT BINDING APPROACH

A. Introduction

Fitting of experimental wave vectors of nanoscale atomic clusters have shown a one-dimensional (1D) free electron band dispersion relation.\textsuperscript{1,2,3} The 1D quantum potential well has been proposed to describe the confinement of the electrons and the local conductivity determined by the superposition of wave functions.\textsuperscript{1,2,3} In contrast to a superposition of wave functions of the 1D potential well,\textsuperscript{1,2,3} the experimental results are described here by the site-dependent occupation number along of
the chain. We have used the tight binding Hamiltonian

$$H_0 = -t \sum_{i,\alpha} (c_{i\alpha}^\dagger c_{i+1\alpha} + h.c),$$

(1)

where $c_{i\alpha}^\dagger (c_{i\alpha})$ are the creation (annihilation) operators for the electrons of spin $\alpha$ at site $i$ and $t$ is the nearest neighbor hopping integral representing the overlap of electron wave functions. To gain a quantitative picture of the on site-dependence on a chain of $N$ atoms, we have computed the local occupation number

$$n_m(i) = \langle \Psi_m | \hat{n}_i | \Psi_m \rangle / N,$$

(2)

where $\hat{n}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}$, $\hat{n}_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha}$ and $|\Psi_m\rangle$ is the $m$th eigenvector with energy $E_m$ of $H_0$.

As illustration of our approach, we analyze the experimental data of the eigenenergies for chains of three, five, seven, nine and fifteen atoms extracted of Ref.\textsuperscript{1}. We have fitted the data taking the experimental ground-state energies and considering $t$, in the tight binding Hamiltonian of Eq. 1, conveniently to obtain the experimental bandwidths. The theoretical and experimental energy spectra are shown in Figs. 1a-e. The experimental data are reproduced. The electron hopping strength as function of the chain length can be observed in Fig. 1f. Note that, as the chain length increases the electronic hopping decreases. The change of hopping amplitudes should be caused by changes of the underlying atom chains.

In the following will investigate the question of the length distribution of atom chains.
B. Length distribution

Recent results on the distribution of chain segments of gold deposited on a Si surface reveal a relation between the chain length and the cohesive energy. The size distribution is characterized by a strong peak for a length of one atom and even-odd oscillations, where even chain lengths are favored over odd lengths. We have obtained a direct relation between this experimental result and the local electronic density of the tight binding model on a finite open chain. We find that on some sites the probability of finding electrons in the excited energy levels is zero. We also observe that these sites correspond to positions that divide the chain in $m$ subchains of equal length. The delocalized electronic structure determines the stability of the atom chain. The cohesive energies are a consequence of the local electronic structure.

In particular, we observe that the sites with zero probability to find electrons on odd chains are not binding, and result in a larger probability for breaking chains. To address this problem we propose a simple model. First, we consider the distribution of chain lengths for a completely random distribution of defects to be $\rho(1 - \rho)^N$, where $\rho$ is the defect density. Since chains are fabricated at temperature $T \sim 1000^\circ$C and considering $t \sim 1$ eV, it is relevant to evaluate the canonical average for any quantity $x$ as

$$\langle x \rangle \equiv \sum_i x_i \exp(-E_i/k_BT)/Z,$$

(3)

where $Z$ is the partition function. Next, we assume that there are quantum states breaking a chain of length $m$ into $g$ pieces of length $N$. It follows that $g \equiv g_{m,N} = (m + 1)/(N + 1)$ and we can write the distribution of chain lengths as

$$P(N) = A \sum_{m=1}^{\infty} \rho(1 - \rho)^m \langle x(m, N) \rangle,$$

(4)

where $A$ is a normalization constant, $q_{m,N} = g_{k,N} \delta_{k,N}$, $k = k(m, i)$ is a non-trivial function obtained numerically, and $\delta_{k,N}$ is the Kronecker’s delta.

Fig. 2 shows the experimental data, extracted from Ref. 2, and our theoretical chain lengths distribution for low and medium defect densities. The even-odd oscillations are clearly visible. Notably, the present model captures qualitatively the experimental chain lengths distribution, considering only the electronic structure effects. The quantitative disagreement between theory and experiment is due to the coupling of the electronic structure with the substrate. This coupling was observed in Ref. 2 using photoemission measurements of the electronic scattering vectors at the Fermi surface of the surface states.

Furthermore, a mechanism for the change in chain length obtained by comparing STM images of the same sample region taken at different voltages is also confirmed by our results. Taking different voltages in STM, the system can fall into an energy level that singles out to a position, which divides the chain in subchains. An additional nearest-neighbor interaction, reflecting the end states in the chains, was used to describe this effect in Ref. 2 and has been already observed in other STM topography data.

III. ELECTRON-ELECTRON INTERACTION

In addition to the tight binding model, containing one electron, it is possible to vary the band filling of chain structures. A strong electronic interaction was found for small chains of Mn on CuN, and the STM data were consistent with the Heisenberg model results. In this case, the effect of electron-electron interaction is particularly important.

The possibility of explaining some STM measurements by the tight binding model and others measurements by the Heisenberg model indicates that we can use a description using the Hubbard model. The 1D Hubbard model is defined by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow},$$

(5)

where $U$ is the on-site Coulomb (electron-electron) interaction.

Solutions for the 1D Hubbard model are known since the sixties. The local behavior of the physical quantities is however not completely known. Only partial informations are available. For example, the spatial dependence of the occupation number and of the magnetization was calculated for the 1D Hubbard model with...
open boundary conditions at zero temperature combining numerical computations from density-matrix renormalization group and Bethe-Ansatz methods. It is important to observe that Friedel oscillations for the density and the magnetization in open Hubbard chains have been obtained in previous works (see and references therein), however, the focus of these studies has been to analyze the physical properties of systems having macroscopic size.

We perform exact calculations of physical quantities of 1D systems having \( N \) atoms described by the Hubbard model. We use the standard direct diagonalization method and impose open boundary conditions in order to break the translational symmetry.

We have found in a half-filled band for \( U = 0 \) that the occupation number of the ground state is site-independent. For \( U > 0 \) this result is valid for all states. This is relevant in order to evaluate the thermodynamic quantity \( \langle n(i) \rangle \). We obtain in a half-filled band that \( \langle n(i) \rangle = 1/N \) for all sites \( i \), temperatures \( T \) and couplings \( U > 0 \). This is a valuable result because the sites are not equivalent due to the use of open boundary conditions. For other than half-filled bands, we observe a site-dependence of \( n_m(i) \). For a quarter-filled Hubbard band we have found a rich dependence on \( U, m, i \) and \( T \).

Fig. 3a presents the topography of \( n_0(i) \) versus \( U/t \) for a chain of 8 sites in the quarter-filled band for the temperature \( T = 0 \). At low values of \( U/t \), the intermediate atoms have a greater value than average and the end and central atoms have smaller values. Here, the probability of finding electrons on the intermediate atoms is higher. The site-dependence decreases if the electron-electron interaction increases. For \( U/t \rightarrow \infty \) the site-dependence disappears and for all \( i \) we find \( n_0(i) = 1/8 \). We can alternatively fix \( U/t \) and vary the temperature in order to cover the other energy states. Fig. 3b shows this for \( U/t = 8 \) (other values of \( U/t \) give similar results). The effect of increasing the temperature is equivalent to an increase of \( U/t \). Large temperature destroys the site-dependence of the charges at the chain. It is important to comment that while this statement appears true for the local occupation number, there are other quantities, such as intersite spin correlations, that may not follow this rule.

For the magnetic properties of finite chains, first-principle calculations have shown that for small chains the spin moment depends on position and cluster length. For example, for Co chains on Pt(111), the spin moments at the end atoms are higher than those at the central atoms and the spin moment of the central atom was found to decrease if the chain size increases. Results of the present study are illustrated in Fig. 4. We have studied the local spin number

\[
S_m(i) = \langle \Psi_m | \hat{S}^z_i | \Psi_m \rangle,
\]

where \( \hat{S}^z_i = (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow})/2 \) at site \( i \).

The local spin number \( S_0(i) \) versus the position \( i \) for a chain of 7 sites, for the half-filled band and temperature \( T = 0 \), can be observed for different total spins \( S = \sum_i S_0(i) \) and \( U/t = 8 \). For \( S = 1/2 \) the alternate sign of \( S_0(i) \) for odd and even position gives evidence for an antiferromagnetic structure. The cases \( S > 1/2 \) have a ferromagnetic structure, since all \( S_0(i) \) have the same sign. Site-independence is found for \( S = 7/2 \). On the other hand, when \( S \) is between the minimal and maximal values we find a site-dependence for \( S_0(i) \), whose amplitude still alternates but not sufficiently to change its sign. For \( S = 5/2 \) we obtain that \( S_0(i) \) is higher at the end atoms than at the central atoms as has been found for Co chains on Pt(111). An important aspect is the influence of the band filling and the cluster length. In particular, we have found that for the case of even total electron number \( (n_m = \sum_i n_m(i)) \) the \( S_m(i) \) is site-independent in all \( m \) states. \( \langle S(i) \rangle = 0 \) for all sites \( i \), temperatures \( T \) and couplings \( U \). Considering \( N \) even, using that \( \langle n(i) \rangle = 1/N \) in the half-filled band and \( \langle S(i) \rangle = 0 \), we have that the canonical ensemble averages are site-independent, like in mean-field, and \( \langle n_1(i) \rangle = \langle n_1(i) \rangle = 1/(2N) \) indicating that the open finite even chain is paramagnetic in the half-filled band. It is important to mention that we find site-independence although the system has no translational symmetry. The situation for odd finite chains is different. In this case \( \langle n(i) \rangle = 1/N \), but \( \langle S(i) \rangle \) has a complex site-dependence.

For the ground state, at \( U = 0 \) we obtain a structure in which \( S_0(i) = 1/(N + 1) \) and on the nearest-neighbor sites \( S_0(i) = 0 \) \( \langle S(i) \rangle = 0 \langle S(i) \rangle = 1/2 \). At \( U > 0 \) we observe an antiferromagnetic structure.

Finally, we explore the dependence of the site-dependent spin on the coupling \( U \). Fig. 4b shows \( S_0(i) \) for the quarter-filled band versus \( i \) for a chain of 6 atoms and typical \( U/t \) values. The ground state has \( S = 1/2 \). Here, we show the case \( S^z = 1/2 \). For low \( U/t \) all \( S_0(i) \) have the same sign favoring a ferromagnetic order and the higher \( S_0(i) \) values are at intermediate atoms and the smaller at the central atoms. Increasing \( U/t \) the central atoms assume negative values for the spin and the higher \( S_0(i) \) shift to the end atoms following a \( \uparrow \downarrow \downarrow \downarrow \downarrow \downarrow \) magnetic stripe structure.

The control and manipulation of the spin rather than the charge of electrons in STM could show the very rich behavior of the local magnetic properties presented here. It would be of interest to explore the possibility of obtaining experimental results in the context of magnetic force microscopy (MFM) devices. This would generate images that are sensitive to the spin polarization of the electrons. The site-dependent magnetic moment (spin) shown here could be confirmed by these experiments.

IV. CONCLUSION

We have shown that the spatial peak structure of STM constant-current topography can be explained in terms of the site-dependent occupation number. We interpret the even-odd oscillation of the length distribution of atom
FIG. 4: (a) Site-dependent spin $S_0(i)/S$ versus the position $i$ for a chain of 7 sites, for a half-filled band, $U/t = 8$ and different total spin $S = \sum_i S_0(i)$. (b) $S_0(i)$ for a chain of 6 sites for a quarter-filled band versus position $i$ for temperature $T = 0$ and $U/t = 0, 2, 8, 16$ and 50.

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