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# Calculation of conductance spectra of silver clusters on graphite

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**ABSTRACT** The transport properties of  $Ag_n$  clusters,  $40 < n < 100$ , deposited on crystalline graphite and probed with a tunneling tip are analyzed by using non-equilibrium Green's functions. Current–voltage characteristics are computed accounting for self-consistent charge redistribution in the cluster caused by coupling to the surface and the external bias. The differential conductance is compared to the density of states of the supported clusters at equilibrium, highlighting the effects of charging and substrate properties on the measured spectrum.

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## 1 Introduction

During recent years, considerable progress has been achieved in the experimental and theoretical study of transport properties of nanostructures and (macro)molecules. Current–voltage ( $I$ – $V$ ) characteristics of, for instance, molecular bridges, single molecules, molecular wires and carbon nanotubes were measured and theoretically described [1–6].

In the case of clusters supported on surfaces, however, the understanding of transport properties and differential conductance curves is still rather poor, since both experimental and theoretical investigations turn out to be more difficult to apply than in the case of well-defined nanostructures and molecules. The theoretical modeling has been limited to a qualitative description of the variation of peak-level spacing with cluster size [7, 8], since even for relatively small supported clusters the geometric structure is not known in detail. Another difficulty is that for metallic clusters on surfaces a finite external applied bias can easily lead to charge redistributions inside the cluster and to charge transfer to the surface. Moreover, the surface must be considered on a similar level of accuracy as the cluster. Due to these problems there are no concrete predictions of densities of states (DOS),  $I$ – $V$  characteristics and differential conductances of clusters supported on surfaces so far.

In this paper we present a self-consistent theoretical approach based on an approximation of density functional theory (DFT), which is able to handle the problem of quantum electron transport through clusters supported on surfaces. The method allows us to describe different non-equilibrium sit-

uations and experimental setups. We analyze here the case of a scanning tunneling microscopy (STM) measurement, i.e. such that when a finite bias voltage is applied between the surface and a probing tip, a tiny tunneling current flows across the gap that separates the tip and the sample. The differential conductance  $dI/dV$  gives the information on the DOS of the sample, allowing us to perform spectroscopy measurements, a technique which goes under the name of scanning tunneling spectroscopy (STS).

The paper is organized as follows. In Sect. 2 we describe the method used and the relevant equations to be solved. In Sect. 3 we present and discuss the results, showing the importance of performing the calculations self-consistently.

## 2 Theory

We use a microscopic approach based on non-equilibrium Green's functions. In order to allow for tackling clusters with a few hundred atoms these Green's functions are written in terms of a DFT-based tight-binding model. The single-particle wave functions are approximated by an expansion in an atomic-like orbital basis [9], which is determined by solving the Kohn–Sham equations of the individual atoms within the local density approximation. The resulting tight-binding (TB) Hamiltonian consists of only two center integrals which can be obtained exactly by using a Slater-type function basis for the atomic orbitals. This scheme is refined to include charge self-consistency by expanding the DFT energy functional to the second order in the charge-density fluctuations [13, 14]; such an expansion leads to the derivation of an additional term to complete the TB Hamiltonian, which contains the contribution of the net atomic charges on the local effective potential. As in a full DFT calculation, self-consistency is obtained with iterative methods, such that the local density, given by the sum of the (approximated) Kohn–Sham eigenfunctions, is consistent with the effective potential.

Green's functions provide a convenient tool to calculate measurable quantities like local electron density and total energy. Having fixed some basis set  $\{\varphi_\mu(r)\}$  to represent the Green's function, the matrix  $\varrho$  representing the charge density in the given basis is obtained by simple integration:

$$\varrho_{\mu\nu} = -\frac{1}{\pi} \int_{-\infty}^{E_F} dE \operatorname{Im} [G_{\mu\nu}(E)], \quad (1)$$

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where  $E_F$  is the Fermi level (degenerate case). From the matrix  $\varrho$  one obtains the average occupation number  $n_\mu = \sum_\nu \varrho_{\mu\nu} S_{\mu\nu}$  of orbital  $\mu$ , with  $S_{\mu\nu}$  being the overlap matrix of the atomic orbitals. Note that  $\mathbf{G}(E)$  in (1) refers to the *retarded* Green's function<sup>1</sup>. The great advantage of the Green's function approach to electronic-structure theory is that it allows us to compute the electronic structure of systems which can be partitioned into smaller non-interacting subsystems. In the cluster–surface case, the unperturbed Hamiltonian takes the block-diagonal form

$$\mathbf{H}^0 = \begin{pmatrix} \mathbf{H}_c^0 & 0 \\ 0 & \mathbf{H}_s^0 \end{pmatrix}, \quad (2)$$

where  $\mathbf{H}_c^0$  and  $\mathbf{H}_s^0$  are the Hamilton matrices of the cluster and the surface, respectively. The Green's function is also block diagonal, with the isolated cluster and surface Green's functions  $\mathbf{G}_c^0(E) = [E \mathbf{S}_c^0 - \mathbf{H}_c^0]^{-1}$  and  $\mathbf{G}_s^0(E) = [E \mathbf{S}_s^0 - \mathbf{H}_s^0]^{-1}$ , respectively, where  $\mathbf{S}_c^0$  and  $\mathbf{S}_s^0$  are the overlap matrices. When the interaction is turned on, the Hamilton matrix of the total system  $\mathbf{H}$  and the overlap matrix  $\mathbf{S}$  acquire the off-diagonal block elements  $\delta\mathbf{H}_{cs}$  and  $\delta\mathbf{S}_{cs}$ , which account for the tunneling between the cluster and the surface. The Green's function of the whole system is then obtained from the solution of the Dyson equation [10]

$$\mathbf{G}(E) = \mathbf{G}^0(E) + \mathbf{G}^0(E) [\delta\mathbf{H} - E \delta\mathbf{S}] \mathbf{G}(E), \quad (3)$$

with  $\delta\mathbf{H} := \mathbf{H} - \mathbf{H}^0$  and  $\delta\mathbf{S} := \mathbf{S} - \mathbf{S}^0$ , corresponding to the change in the Hamilton and the overlap matrices. Since we are interested in the electronic properties of the cluster, it is sufficient to compute the cluster part of the Green's function,  $\mathbf{G}_c(E)$ , which is obtained by solving the Dyson equation

$$\mathbf{G}_c = \mathbf{G}_c^0 + \mathbf{G}_c^0 \boldsymbol{\Sigma}_c \mathbf{G}_c, \quad (4)$$

where  $\boldsymbol{\Sigma}_c$  is the self-energy given by

$$\begin{aligned} \boldsymbol{\Sigma}_c(E) &= \delta\mathbf{H}_c + [\delta\mathbf{H}_{cs} - E \delta\mathbf{S}_{cs}] [(G_s^0)^{-1} - \delta\mathbf{H}_s]^{-1} [\delta\mathbf{H}_{sc} - E \delta\mathbf{S}_{sc}]. \end{aligned} \quad (5)$$

The self-energy  $\boldsymbol{\Sigma}_c$  requires the surface Green's function  $\mathbf{G}_s^0$ , which can be calculated with recursion methods [11], and includes the information on the band structure of the substrate, therefore determining the nature of the chemical bonding between the cluster and the surface.

In the simplest approximation one can neglect the relaxation of the electronic structure in the cluster and on the surface due to their mutual interaction, which corresponds to setting  $\delta\mathbf{H}_s = 0$  and  $\delta\mathbf{H}_c = 0$ , while keeping fixed the tunneling terms  $\delta\mathbf{H}_{cs}$  and  $\delta\mathbf{H}_{sc}$ . In contrast to that, the full self-consistent description of the whole system requires the solution of (3), which in principle involves the infinite degrees of freedom of the surface. Here, we neglect charge redistribution on the surface by setting  $\delta\mathbf{H}_s = 0$ , and therefore solve recursively the Dyson equation for the cluster alone, cf. (4), in order to obtain  $\delta\mathbf{H}_c$ . At each iteration step,  $\mathbf{G}_c$  is used to compute the net

atomic charges which are fed into the local effective potential of the Hamiltonian [13, 14], therefore leading to a new cluster Green's function, which provides the density for the next iteration, until convergence is reached. Self-consistency is necessary to account for charge transfer to the bulk solid, which changes the position of the energy levels in the cluster relative to the chemical potential of the substrate.

The expression for the density matrix in (1) is valid only in equilibrium conditions; when the cluster is probed with an STM tip at non-zero bias the charge on the cluster is obtained from the correlation function  $\mathbf{G}_c^<$  defined by

$$\mathbf{G}_c^< = \mathbf{G}_c \boldsymbol{\Sigma}^< \mathbf{G}_c^\dagger, \quad (6)$$

where the lesser self-energy  $\boldsymbol{\Sigma}^<$  depends on the Fermi functions of the surface and the tip  $f_s(E)$  and  $f_t(E)$  and the broadening matrices  $\boldsymbol{\Gamma}_s$  and  $\boldsymbol{\Gamma}_t$ , which account for the interaction with the surface and the tip, are given by

$$\boldsymbol{\Sigma}_c^< = i f_s \boldsymbol{\Gamma}_s + i f_t \boldsymbol{\Gamma}_t, \quad (7)$$

where

$$\boldsymbol{\Gamma}_s = i [\boldsymbol{\Sigma}_{cs} - \boldsymbol{\Sigma}_{cs}^\dagger], \quad \boldsymbol{\Gamma}_t = i [\boldsymbol{\Sigma}_{ct} - \boldsymbol{\Sigma}_{ct}^\dagger]. \quad (8)$$

The non-equilibrium analogue of (1) reads

$$\varrho_{\mu\nu} = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \mathbf{G}_{\mu\nu}^<(E), \quad (9)$$

and can be used to relax self-consistently the electronic charge in the cluster, as in the equilibrium case. The usual procedure to obtain the current starts from the equations of motion for the Green's functions  $\mathbf{G}_{\mu\nu}^<$ . In the case of coherent transport the stationary current can be calculated as [12]

$$I = \frac{e}{h} \int dE (f_t - f_s) T(E), \quad (10)$$

with the energy-dependent transmittance<sup>1</sup>

$$T(E) := \text{Tr} [\mathbf{G}_c \boldsymbol{\Gamma}_s \mathbf{G}_c^\dagger \boldsymbol{\Gamma}_t]. \quad (11)$$

As in the equilibrium case, the self-consistent charge distribution on the cluster at a finite bias is obtained recursively; in both cases the following main point has to be remarked upon: we are dealing with an open system and thus have to, instead of filling the orbitals according to the Aufbau principle, integrate the Green's functions over the energy  $E$ , cf. (1) and (9), respectively. This task requires some care and can be achieved by taking advantage of the analytic properties of  $\mathbf{G}$  (see for example [15]).

### 3 Results

The first step in our calculations was to determine the cluster geometry and relative position and orientation with respect to the surface. Given the number of atoms in the clusters at hand, and especially because of the presence of a surface, it is not feasible to relax all atomic degrees of freedom. We assume a geometry which agrees with the measured

<sup>1</sup> In order to avoid confusion with many sub- and superscripts, we will always refer to  $\mathbf{G}$  and  $\boldsymbol{\Sigma}$  as the retarded Green's functions and self-energies

width-to-height ratio,  $w/h = 1.4$  [8], with a fcc crystal structure having the lattice constant equal to the Ag bulk value (nearest-neighbor distance 2.983 Å). To define the facets we carry out a Wulff construction (see for example [16]). The top facet is assumed to have a (111) orientation. Figure 1 shows three examples of clusters obtained according to the rules briefly described above.

The positioning of the cluster is defined by keeping its bottom facet parallel to the  $(x, y)$  plane of the ideal graphite surface, allowing for translations in the three axes and rotations around the normal axis  $z$ . We choose a cluster–surface distance of 2.6 Å compatible with the simulations of Ag adatoms and dimers on graphite [17], while we checked that the DOS of the cluster does not change significantly as it is displaced and rotated in the  $(x, y)$  plane, implying that in this case the metal–carbon bonding remains unaffected. Such behavior is consistent with the high mobility observed experimentally for clusters on highly oriented pyrolytic graphite (HOPG) devoid of defects, showing that graphite appears as a fairly uniform surface.

Once the structure, position and orientation of the cluster are assigned, the self-consistent charge distribution is obtained recursively for the equilibrium configuration. We consider a simple model for the STM tip, using an extended Au electrode placed 5 Å away from the top facet of the cluster, so that the interaction remains rather weak. The strong coupling of the cluster with the substrate, on the other hand, leads to charge transfer whose absolute value depends on the location of its energy levels with respect to the chemical potential of graphite; in our calculations we observe that the central part

of the cluster closer to the graphite acquires a positive charge, in contrast to the top and the sides which are negative. The charge imbalance per atom is of the order of  $\pm 0.05$ , resulting in a typical net charge of about +0.2. To what extent this charging may induce structural changes and influence by this the conductance could only be answered by a full quantum molecular dynamics study, which is currently out of reach for clusters on surfaces.

The density of states and the zero-bias transmittance for the three cluster sizes are displayed in Fig. 2, showing a neat correspondence for the peak positions; some enhancing of peak heights in the transmittance curves can be appreciated at energy levels displaced from the Fermi potential, as a consequence of the DOS of the graphite, which increases linearly as one proceeds away from the Fermi level itself.

As a finite voltage is applied between the tip electrode and the graphite surface, we are in a non-equilibrium situation. The external electrical field causes further rearrangement in the cluster charge density, which has to be consistent with the two different chemical potentials of the contacts. As a result, the single-particle levels for the clusters may shift with respect to the equilibrium situation. These shifts are visible in Fig. 3, where we show the DOS superimposed on the differential conductance curve. The substantial match between the two curves is due to the facts that the cluster remains almost in equilibrium with the graphite surface even when some finite bias is applied, and that most of the potential drop occurs in the empty gap between the top of the cluster and the tip.

As a final remark, we would like to point out that the curves displayed in Figs. 2 and 3 exhibit a some-

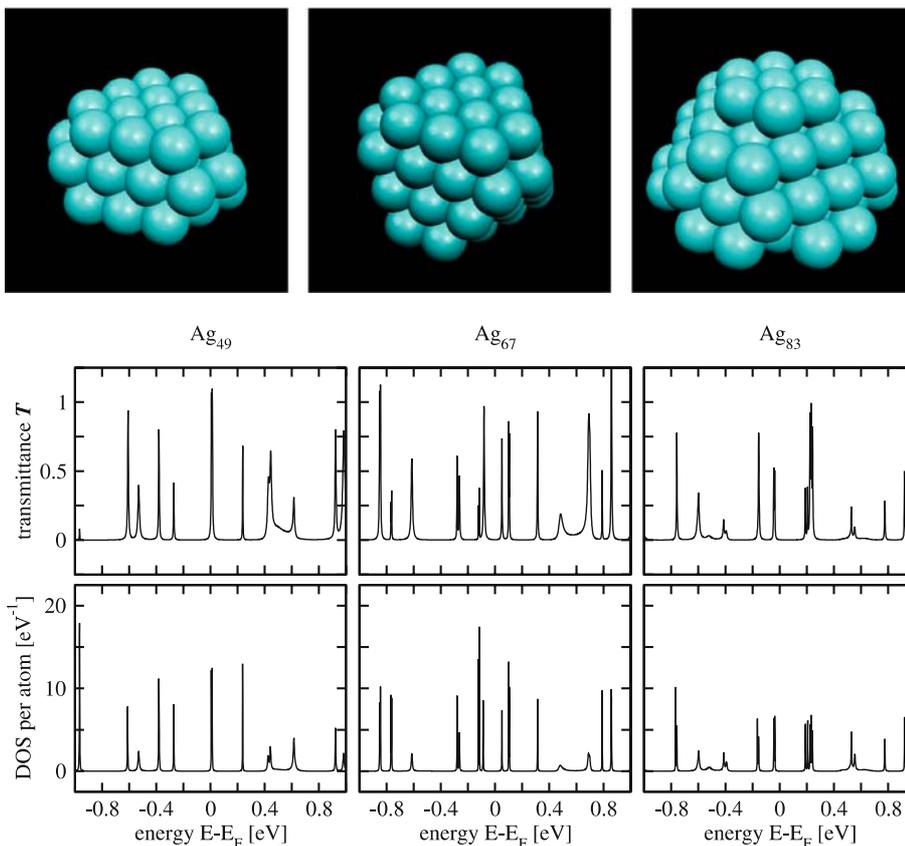
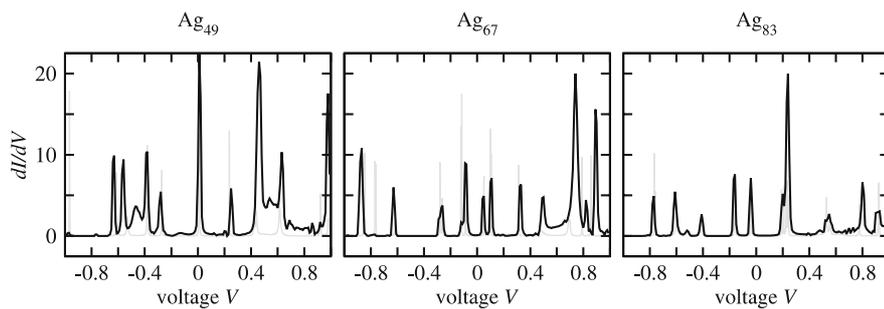


FIGURE 1 Ag cluster geometries with 49 (left), 67 (middle) and 83 (right) atoms obtained assuming bulk lattice spacing and using the Wulff construction

FIGURE 2 Densities of states (lower) and transmittance  $T$  (upper) according to Eq. (11) of Ag<sub>49</sub>, Ag<sub>67</sub> and Ag<sub>83</sub> on graphite



**FIGURE 3** Differential conductance  $dI/dV$  curves (black lines) of  $Ag_{49}$ ,  $Ag_{67}$  and  $Ag_{83}$  on graphite. For comparison we have added the DOS of the clusters (gray lines) already shown in the lower part of Fig. 2. The conductance values have been rescaled to be comparable with the DOS curves

what richer structure when compared to low-temperature STS measurements for Ag clusters grown on nanopits on HOPG [8]. This discrepancy should probably be attributed to a stronger cluster–surface coupling due to contact with the pit edges on the substrate or to the particular chosen shape of our tip, and will be the subject of further investigations.

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