

## Anderson-type model for a molecule adsorbed on a metal surface

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**Abstract.** – We investigate a modified Anderson model to study the local density of states (LDOS) of a molecular wire adsorbed on a metal. Using a self-consistent mean-field-type approach, we find an exponential decay of the LDOS along the molecule. A repulsive on-site interaction on the molecule suppresses the tunneling and decreases the characteristic decay length.

*Introduction.* – In the last decade, a lot of progress has been made in the theoretical and experimental investigation of nanostructures like quantum dots and quantum wires [1]. These structures are produced by lithography. Using this very flexible technology, a large variety of different structures with different geometries has been made. Simple dots, multiple dots, dot arrays and the corresponding leads have been realized both using metals and semiconductors. A disadvantage of lithographic methods is the presence of fluctuations in shape and size of these structures; they are unavoidable because of errors in writing the mask and because of the stochastic nature of the etching process.

The idea to use molecules or supramolecular structures as quantum wires and quantum dots has been around for quite a while, see ref. [2] for an early suggestion of a molecular rectifier and refs. [3, 4] for recent reviews. Powerful chemical synthesis methods are available that allow the production of atomic and molecular clusters with linear dimensions of up to 5 nm, *i.e.*, they are approaching the lowest linear dimensions of nanostructures produced by lithography. It is a fascinating idea that such clusters which would have custom-made electronic properties could be included in nanostructures and replace, say, a quantum dot. Different copies of these systems would be identical in structure and properties (*e.g.*, there is no difference in the composition of different C<sub>60</sub> molecules). First steps in the direction of this “bottom-up approach” are under way in a number of labs around the world. Scanning probe techniques have been used to arrange atoms on a substrate in arbitrary ways [5, 6]. A particularly impressive example is the “quantum corral” [7], a circularly shaped structure of Fe atoms on a Cu(111) surface that may be considered a precursor of a device. Carbon nanotubes have been contacted and proven to exhibit Coulomb-blockade behavior [8, 9]. A new kind of transistor whose central element is a C<sub>60</sub> molecule has been proposed [10]. The theory of conduction through molecular wires has been studied by a number of groups (see, *e.g.*, refs. [11–15]). Also, the thermal conduction through molecular wires has been investigated [16]. Recently, the coupling of a molecule to a metal has been studied both experimentally and theoretically [17, 18].

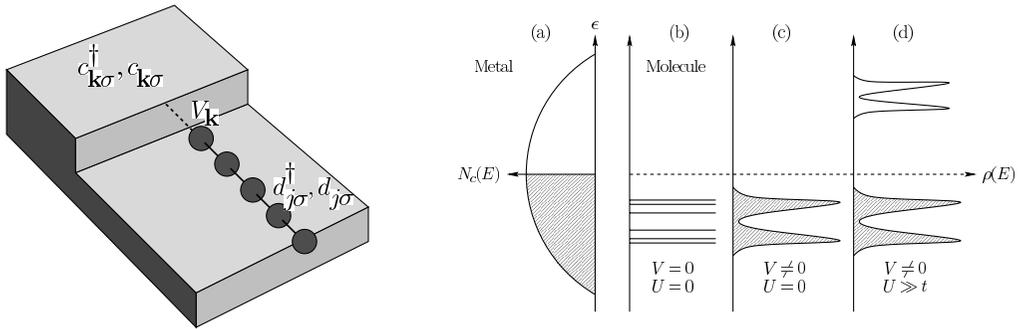


Fig. 1 – Left part: schematic view of the system. We describe the molecule by a tight-binding model, *i.e.*, a discrete lattice of atomic sites. The coupling of the molecule to a metal consisting of non-interacting electrons in a conduction band is assumed to be small and characterized by the tunneling amplitude  $V_{\mathbf{k}}$ . Right part: sketch of the energy spectrum of the model. (a) Unperturbed density of states  $N_c(E)$  of the metal. (b)-(d) Density of states  $\rho(E)$  at a typical molecular site. (b) Isolated molecule ( $V_{\mathbf{k}} = 0$ ) without electron-electron interaction ( $U = 0$ ). (c) Molecule without interaction coupled to the metal. The coupling broadens the discrete molecular levels. (d) Molecule in the presence of strong electron-electron interaction ( $U \gg t$ ) coupled to the metal. In the half-filled case (one electron per site), the interaction will lead to the formation of an upper Hubbard band.

A central problem facing the use of molecules as electronic devices is the question of how to contact them in a reproducible way. An interesting answer to this question was given in a recent experiment [19] in which a custom-designed “lander” molecule [20] was adsorbed on a (111) copper surface. The molecules can be thought of as consisting of an aromatic platform and four spacer “legs”. The spacer legs keep the main board at such a distance from the metal surface that the aromatic part is electronically decoupled from the surface.

The molecules self-assembled perpendicularly to a step on the surface, thereby forming a contact between the metal and the aromatic board (the length of the legs was chosen to be comparable to the step height). A scanning-tunneling microscope (STM) was used to scan along the surface and the molecule, and it was found that the tunneling conductance decayed in an exponential way along the molecule.

In this paper, we would like to study a (relatively) simple model for the molecule at the metal step. In contrast to the quantum-chemical calculations provided in [19] that take into account the precise structure of the lander molecule, we propose to use a modified Anderson model to describe this situation. The “impurity” of the new model is spatially extended, *i.e.*, contains internal degrees of freedom not present in the standard Anderson model. The aim will be to calculate the local density of states of an extended structure (the molecule) using a Green’s function method. The molecule will be approximated by a (finite) one- or two-dimensional tight-binding lattice with a Hubbard-like interaction. Our goal is to gain a *qualitative understanding* of the physical problem and its phenomenology (as opposed to quantum-chemical calculations for *specific* molecules) to be able to propose and analyze more complicated (*e.g.*, multiply connected) structures in the future.

*Model.* – The system we have in mind is shown in fig. 1. Our model is defined by a Hamiltonian that consists of three parts,  $H = H_c + H_d + H_T$ . The metal to which the molecular wire is attached is described by non-interacting electrons in a conduction band

$$H_c = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} , \quad (1)$$

where  $\mathbf{k}$  and  $\sigma = \uparrow, \downarrow$  denote electron wave vectors and spins, respectively. The single-electron energy  $\epsilon_{\mathbf{k}}$  is measured with respect to the Fermi energy ( $\epsilon_F = 0$ ). The molecular wire is assumed to be a one-dimensional lattice of  $L$  atomic sites and is described within the Hubbard model

$$H_d = \sum_{i,j=1}^L t_{ij} d_{i\sigma}^\dagger d_{j\sigma} + U \sum_{j=1}^L n_{j\uparrow} n_{j\downarrow}. \quad (2)$$

The parameters that enter here are the on-site electron-electron interaction  $U$  and the matrix elements  $t_{ij} = \epsilon_d \delta_{ij} - t \delta_{i,j\pm 1}$ , where  $\epsilon_d$  is the on-site energy of the single-particle level at each site and  $t$  is the hopping element between nearest neighbors. The coupling of the wire to the metal is assumed to be small so that we can describe it by the tunneling amplitude  $V_{\mathbf{k}}$  of the electron in the state  $(\mathbf{k}, \sigma)$  to the first site  $j = 1$ :

$$H_T = - \sum_{\mathbf{k}\sigma} \left( V_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger d_{1\sigma} + \text{h.c.} \right). \quad (3)$$

The model defined by  $H$  is a generalization of the Anderson impurity model: for  $L = 1$ , the molecule reduces to a localized level, and (3) is the hybridization term of the Anderson impurity model.

The qualitative nature of the spectrum of the system is shown in the right part of fig. 1. We characterize the metal by a model density of states  $N_c(E)$  to be discussed below and shown schematically in (a). If the molecule is not coupled to the metal,  $V = 0$ , its spectrum consists of discrete levels as shown in (b). Coupling the molecule to the metal broadens the spectral lines as shown in (c). If we assume a filling of one electron per site, the presence of strong on-site interactions leads to the formation of a Mott-Hubbard gap as shown in (d).

We will use the imaginary-time path-integral formalism at finite temperature  $k_B T \equiv 1/\beta$  (see, *e.g.*, ref. [21]). In this formalism, the Euclidean action is given by

$$S^E = \int_0^\beta d\tau \left( \sum_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^\dagger \partial_\tau c_{\mathbf{k}\sigma} + \sum_{j\sigma} d_{j\sigma}^\dagger \partial_\tau d_{j\sigma} + H \right), \quad (4)$$

and we want to calculate the thermal Green's function

$$\mathcal{G}(j\sigma, k\sigma'; \tau) = - \left\langle T_\tau d_{j\sigma}^\dagger(0) d_{k\sigma'}(\tau) \right\rangle \quad (5)$$

and its Fourier transform defined by  $\mathcal{G}(j\sigma, k\sigma'; i\omega_n) = \int_0^\beta d\tau e^{i\omega_n \tau} \mathcal{G}(j\sigma, k\sigma'; \tau)$ , where  $\omega_n \equiv (2n+1)\pi/\beta$  with  $n$  integer are the Matsubara frequencies.

First, we consider the non-interacting case,  $U = 0$ . In this case, the Euclidean action (4) is quadratic both in  $c_{\mathbf{k}\sigma}$  ( $c_{\mathbf{k}\sigma}^\dagger$ ) and  $d_{j\sigma}$  ( $d_{j\sigma}^\dagger$ ), and it follows that  $\mathcal{G}(j\sigma, k\sigma'; i\omega_n) = \delta_{\sigma\sigma'} \mathcal{G}(j, k; i\omega_n)$ ,

$$\mathcal{G}^{-1}(j, k; i\omega_n) = \mathcal{G}_0^{-1}(j, k; i\omega_n) - \Sigma_c(j, k; i\omega_n), \quad (6)$$

or, more explicitly,

$$\mathcal{G}(i, j) = \mathcal{G}_0(i, j) + \frac{\mathcal{G}_0(i, 0) \Sigma_c(0, 0) \mathcal{G}_0(0, j)}{1 - \mathcal{G}_0(0, 0) \Sigma_c(0, 0)}. \quad (7)$$

The unperturbed (non-interacting, isolated) Green's function is given by

$$\mathcal{G}_0^{-1}(j, k; i\omega_n) = i\omega_n - t_{jk}. \quad (8)$$

In eqs. (6) and (7), the coupling to the metal manifests its effect on the wire through the self-energy

$$\Sigma_c(j, k; i\omega_n) = \delta_{j1}\delta_{k1} \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} \frac{\Gamma(\epsilon)}{i\omega_n - \epsilon}. \quad (9)$$

The effect of the metal on the molecular wire is given by the function

$$\Gamma(E) \equiv -2 \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \text{Im} G_c^{\text{R}}(\mathbf{k}, E), \quad (10)$$

where  $G_c^{\text{R}}(\mathbf{k}, E)$  is the retarded Green's function for the (unperturbed) metal. In the simplest case in which the energy dependence of the tunneling amplitude  $V_{\mathbf{k}}$  is not too large,  $V_{\mathbf{k}} \approx V$ , (10) can be further reduced to an expression directly proportional to the density of states in the metal  $N_c(E)$ :  $\Gamma(E) = 2\pi V^2 N_c(E)$ .

The local density of states (LDOS) at the  $j$ -th site is then given by the analytic continuation of the thermal Green's function

$$\rho(j, E) = -\frac{2}{\pi} \text{Im} \mathcal{G}(j, j; i\omega_n \rightarrow E + i0^+). \quad (11)$$

The factor 2 accounts for the contributions from the two spin components.

We now turn to the opposite limit in which the electron-electron interaction on the molecule is very strong;  $U \gg t$  [22]. In this case, exact solutions are only available in special cases; the isolated molecule ( $V_{\mathbf{k}} = 0$ ), *i.e.*, the usual Hubbard model [23] and the single-site molecule ( $L = 1$ ), *i.e.*, the usual Anderson impurity model [24]. There are many approximation methods for the Hubbard model or the Anderson model (see ref. [25] for a recent review), and we will adopt a self-consistent mean-field approximation [21].

We start with the strong- $U$  limit of  $H_d$  in (2), *i.e.*, the  $t$ - $J$  Hamiltonian [26]

$$H_d \simeq \sum_{ij} t_{ij} d_{i\sigma}^{\dagger} d_{j\sigma} - \frac{1}{U} \sum_{ijk} t_{ij} (d_{i\uparrow}^{\dagger} d_{j\downarrow}^{\dagger} - d_{i\downarrow}^{\dagger} d_{j\uparrow}^{\dagger}) t_{jk} (d_{j\downarrow} d_{k\uparrow} - d_{j\uparrow} d_{k\downarrow}) \quad (12)$$

within the reduced Hilbert space without doubly occupied sites. The second term in (12) can be made quadratic in  $d_{j\sigma} (d_{j\sigma}^{\dagger})$  by means of the Hubbard-Stratonovich transformation introducing the auxiliary field  $\Delta_j$  to get the molecular part (corresponding to  $H_d$ ) in the Euclidean action (4)

$$S_d^{\text{E}} = S_{\Delta}^{\text{E}} + \int_0^{\beta} d\tau \sum_{ij} \hat{d}_i^{\dagger} \left[ \delta_{ij} \partial_{\tau} + t_{ij} \hat{\tau}_3 - \hat{\Delta}_{ij} \right] \hat{d}_j, \quad (13)$$

where  $\tau_3$  is the Pauli matrix and  $S_{\Delta}^{\text{E}} = \int_0^{\beta} d\tau U \sum_j |\Delta_j|^2$ . In eq. (13), we have introduced a two-component spinor representation

$$\hat{d}_j \equiv \begin{bmatrix} d_{j\uparrow} \\ d_{j\downarrow} \end{bmatrix}, \quad \hat{\Delta}_{ij} \equiv t_{ij} \begin{bmatrix} 0 & \Delta_i + \Delta_j \\ \Delta_i^* + \Delta_j^* & 0 \end{bmatrix}. \quad (14)$$

In this representation, the Green's function in eq. (5) also has a matrix form  $\hat{\mathcal{G}}(i, j; \tau) = -\langle T_{\tau} \hat{d}_i(0) \hat{d}_j^{\dagger}(\tau) \rangle$ . After integrating out the fields  $c_{\mathbf{k}\sigma}$  and  $c_{\mathbf{k}\sigma}^{\dagger}$ , the Euclidean action can be written as

$$S^{\text{E}} = S_{\Delta}^{\text{E}} - \int \int_0^{\beta} d\tau d\tau' \hat{d}_i^{\dagger}(\tau) \hat{\mathcal{G}}^{-1}(i, j; \tau - \tau') \hat{d}_j(\tau'), \quad (15)$$

where the Green's function  $\mathcal{G}$  is given by the Dyson equation

$$\widehat{\mathcal{G}}^{-1}(j, k; i\omega_n) = \widehat{\mathcal{G}}_0^{-1}(j, k; i\omega_n) - \widehat{\Sigma}_c(j, k; i\omega_n) - \widehat{\Sigma}(j, k; i\omega_n), \quad (16)$$

with the new self-energy term  $\widehat{\Sigma}(i, j; \tau) = -\delta(\tau)\widehat{\Delta}_{ij}(\tau)$ . Here  $\mathcal{G}_0$  in (8) and  $\Sigma_c$  in eq. (9) have been extended to matrix form in a trivial way:  $\widehat{\mathcal{G}}_0 = \mathcal{G}_0\hat{\tau}_0$  and  $\widehat{\Sigma}_c = \Sigma_c\hat{\tau}_0$ , where  $\tau_0$  is the identity matrix.

So far no approximation has been made and the formal expression for the Euclidean action in eq. (15) is exact. The interaction effect is correctly incorporated through the self-energy term  $\widehat{\Sigma}$  (whereas the effect of the metal is again manifested by  $\widehat{\Sigma}_c$ ) as long as the integration over the field  $\Delta_j$  is performed properly. At this point, we make our main approximation and neglect the fluctuations in the field  $\Delta_j$ . We first assume a particular realization of the field  $\Delta_j$  in the Dyson equation (16) and then determine  $\Delta_j$  within the stationary-phase approximation. Iterating this procedure allows us to determine  $\Delta_j$  and the Green's function self-consistently. Moreover, the self-consistency equation

$$\Delta_i = \frac{1}{U} \sum_j t_{ij} \langle d_{i\downarrow} d_{j\uparrow} - d_{i\uparrow} d_{j\downarrow} \rangle \quad (17)$$

corresponding to this procedure, gives us a physical interpretation of the field  $\Delta_j$ :  $\Delta_j$  measures the spin-singlet correlation between the  $j$ -th site and its neighboring sites. It is clear that in the limit  $U \rightarrow \infty$ ,  $\Delta_j \approx 2t/U$  unless  $j$  is too close to the boundaries. Finally, the LDOS can be obtained from the diagonal components of the retarded Green's function  $\widehat{G}^R(j, k; E) = \widehat{\mathcal{G}}(j, k; i\omega_n \rightarrow E + i0^+)$ :

$$\rho(j, E) = -\frac{1}{\pi} \text{Im} \left[ \widehat{G}_{11}^R(j, j; E) + \widehat{G}_{22}^R(j, j; -E) \right]. \quad (18)$$

*Results.* – We will now report specific results on the LDOS of the molecular wire and discuss their physical implications. For the density of states (DOS) in the metal, we adopt the model functional form  $N_c(E) = N_c(0)(1 - E^2/W_c^2)$ . The parameters  $N_c(0)$  and  $W_c$  specify the DOS at the Fermi energy and the width of the conduction band, respectively. The self-energy contribution (9) from the coupling to the metal is then given by

$$\Sigma_c(j, k; E) = \delta_{j1}\delta_{k1} V^2 [\alpha_c(E) - i\pi N_c(E)], \quad (19)$$

with  $\alpha_c(E)$  defined by

$$\alpha_c(E) = N_c(0) \left[ \frac{2E}{W_c} + \left( 1 - \frac{E^2}{W_c^2} \right) \ln \left| \frac{E/W_c + 1}{E/W_c - 1} \right| \right]. \quad (20)$$

All results shown in this work will be generated using the values  $\epsilon_d = -4t$ ,  $V = 0.1t$ ,  $W_c = 40t$ , and  $N_c(0) = 10/t$ . The other parameters will be specified as needed. We also remark that we only investigate the lower band, *i.e.*, the band below the Mott-Hubbard gap, in the interacting case.

In fig. 2 we plot typical LDOS curves at three different sites ( $j = 1, 3$ , and  $5$ ) on a molecule with size  $L = 10$  and on-site interaction  $U = 10t$ . The structures get sharper as  $U$  increases [27] because tunneling is blocked, see the discussion below. At a given site, the LDOS decays rapidly outside the band.

Figure 3 shows the spatial dependence of the LDOS along molecules with sizes  $L = 10$  and  $20$ , respectively, both for the non-interacting (open circle) and interacting (solid circle) case.

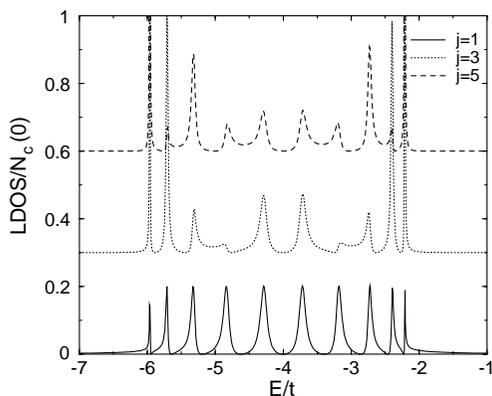


Fig. 2 – Local density of states at site  $j$  for  $L = 10$  and  $U = 10t$ . Solid line:  $j = 1$ , dotted line:  $j = 3$  (shifted upwards by 0.3), dashed line:  $j = 5$  (shifted upwards by 0.6).

The LDOS has been calculated at the fixed energy  $E = -2t$ , slightly above the upper edge of the band (remember that at the parameter values chosen below eq. (20),  $E = -2t$  is the upper edge of the band for an infinite tight-binding chain, *i.e.*,  $H_d$  with  $L = \infty$  and  $U = 0$  in eq. (2)). The LDOS decays exponentially with distance from the metal-molecule contact, except for the region close to the boundaries. This reproduces the exponential decay of the STM tunneling conductance in ref. [19]. It also agrees with the expectation that the electron wave function induced by the metal to the molecule should decay in an exponential way. Another interesting conclusion that can be drawn from fig. 3 is the influence of the interaction on the suppression of the LDOS. The characteristic decay length decreases with the interaction  $U$ . This can be interpreted by saying that the strong repulsion by the electrons sitting on (singly occupied) sites tends to block tunneling events from the metal to the molecule. This effectively leads to the suppression of the “hybridization” term  $H_T$ , eq. (3). The suppression of the LDOS by interaction effects does not depend on the choice  $E = -2t$ , however, the spatial scale would be different for different positions of the molecular level. The influence of repulsive interactions was also studied in [28], where it is shown that the suppression is lower

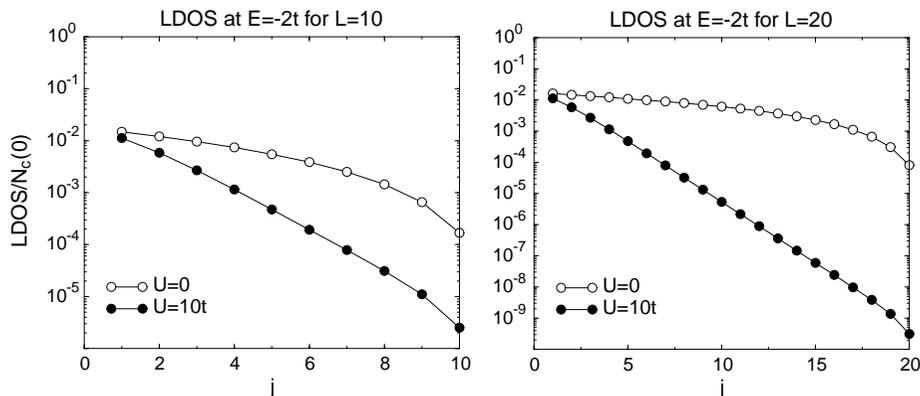


Fig. 3 – Spatial dependence of the local density of states along the molecule. Empty symbols: non-interacting case. Full symbols: interacting case,  $U = 10t$ . Interaction effects on the molecule depress the influence of the metals on the density of states on sites that are far away.

for repulsive interactions than for a dimerization leading to the same value of the gap.

In conclusion, we have calculated the local density of states of a molecule adsorbed to a metal surface using a new Anderson-type model. The LDOS decays along the molecule in an exponential way (like in the experiment [19]) and is suppressed by a local interaction on the molecule. Our formalism provides a qualitative understanding of this and similar experiments. It is able to include local interaction effects and can be used to treat more complicated geometries that will be investigated in future experiments.

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