

Surface impurity problem in the Hubbard model: A renormalization-group study

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In connection with the problem of the chemisorption of an atom into a solid substrate, we solve the one-dimensional Hubbard model with an impurity at one end using a real-space renormalization-group procedure (RS RG). For this purpose we present an extension of the standard RS RG technique that allows handling systems in which there is no translational invariance. We consider the case in which correlations are important both in the adsorbed atom and in the substrate. We show results for the charge transference and binding energy of the impurity as well as the charge rearrangement near the surface.

I. INTRODUCTION

The binding energy and the degree of charge transfer between an adsorbed atom and a solid substrate are two of the most important electronic magnitudes in the description of the chemisorption phenomena. A model extensively used to describe the chemisorption is the Anderson-Grimley-Newns Hamiltonian which includes a correlated impurity coupled to an *uncorrelated* band. This Hamiltonian has been first introduced by Anderson¹ for a single magnetic impurity in a nonmagnetic metal and has been adapted by Grimley² and Newns³ to study the chemisorption problem of adatoms on a metal surface. After these works, based on the Hartree-Fock approximation, a number of different approaches have been used to describe the chemisorption phenomena in which the electron-electron interaction on the metal side is neglected.⁴⁻¹⁴ In a more general context one is interested in considering a situation in which correlations are important in the impurity as well as in the substrate. This can be the case of adsorption of atoms and molecules by narrow band metals (for example H adsorbed on a Ni substrate).

In this paper we will study a generalized Hubbard model that includes correlations both in the substrate and the adsorbate. Based on the real-space renormalization-group technique^{15,16} (RS RG) we extend the procedure to the nontranslationally-invariant case. The RS RG technique is based on an approximation that consists in truncating the Hilbert space to certain lowest-lying states of finite clusters at each step of an iterating procedure. In our case the approximation turns out to be valid in the range of parameters in which the charge at the impurity site fluctuates around 1, in correspondence with the half-filling of the substrate band. Despite this restriction, this situation occurs in most of the realistic chemisorption problems.

We calculate the binding energy of the adsorbed atom at $T=0$, the impurity charge, and also the induced charge redistribution in the first substrate sites. Our results show good quantitative agreement with available experimental results. In Sec. II we present the model and give a description of the procedure. In Sec. III we discuss the results obtained.

II. MODEL AND PROCEDURE

We will consider the following one-dimensional Hamiltonian:

$$H = H_{\text{ads}} + H_{\text{subs}} + H_c. \quad (1)$$

H_{ads} , H_{subs} , and H_c are, respectively, the adsorbate, substrate, and coupling Hamiltonians, given by

$$H_{\text{ads}} = \sum_{\sigma} \left[(W - \mu)n_{0,\sigma} + \frac{U_0}{2}n_{0,\sigma}n_{0,\bar{\sigma}} \right] + \frac{U}{2} - W, \quad (2)$$

$$H_{\text{subs}} = \sum_{i=1}^{\infty} \left[-\mu n_{i,\sigma} + \frac{U}{2}n_{i,\sigma}n_{i,\bar{\sigma}} + t(c_{i,\sigma}^{\dagger}c_{i+1,\sigma} + \text{H.c.}) + \frac{U}{4} \right], \quad (3)$$

$$H_c = \sum_{\sigma} t'(c_{0,\sigma}^{\dagger}c_{1,\sigma} + \text{H.c.}), \quad (4)$$

where W is the atomic level of the adatom, while U_0 and U are respectively the effective Coulomb integrals of the adatom and the substrate. $c_{i,\sigma}^{\dagger}$ ($c_{i,\sigma}$) is the creation (annihilation) operator of an atomic orbital at site i with spin σ . The corresponding occupation number operators are $n_{i,\sigma} = c_{i,\sigma}^{\dagger}c_{i,\sigma}$. t and t' are the hopping matrix elements for electrons in the substrate, and for an electron jumping from the adatom to the substrate, respectively. For the chemical potential $\mu = \frac{1}{2}U$ the substrate Hamiltonian maps into itself under the electron-hole transformation, thus corresponding to the half-filled band case. The constant terms in (2) and (3) were chosen so as to have the $t = t' = 0$ reference state with zero energy.

The real-space Hamiltonian renormalization-group calculation is performed following the works of Jullien *et al.*¹⁵ and Hirsh,¹⁶ with a modification that takes into account the nontranslational invariance of the problem.

We proceed as follows. We divide the lattice into nonoverlapping cells of three sites each and diagonalize exactly the cell Hamiltonian. Note that the cells are all equivalent except for the edge one containing the adsorbed atom (see Fig. 1). We keep the lowest-lying states corresponding to $n=2, 3$, and 4 particles in order to reproduce the level scheme of a single site; i.e., two de-

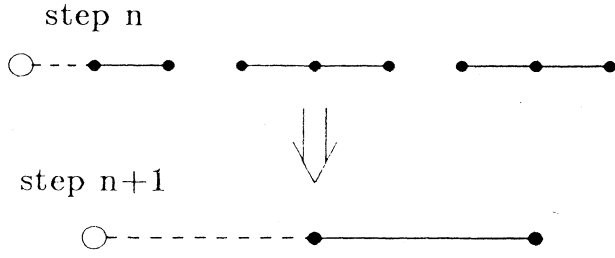


FIG. 1. Schematic representation of the renormalization procedure. The open circle represents the renormalized impurity and the dashed line represents the renormalized coupling matrix element.

generate states for $n=3$ and $S=\frac{1}{2}$, $S_z=\pm\frac{1}{2}$ and one non-degenerate state in each of the subspaces $n=2$ and 4, with $S=0$. We use these states as a new truncated basis and express the new Hamiltonian in terms of block operators. After m iterations we obtain

$$H^{(m)} = H_{\text{ads}}^{(m)} + H_{\text{subs}}^{(m)} + H_c^{(m)}, \quad (5)$$

with

$$H_{\text{ads}}^{(m)} = \sum_{\sigma} \left[(W^{(m)} - \mu^{(m)})n_{0,\sigma} + \frac{U_0^{(m)}}{2}n_{0,\sigma}n_{0,\bar{\sigma}} \right] + D^{(m)}, \quad (6)$$

$$H_{\text{subs}}^{(m)} = \sum_{\sigma} \left[-\mu^{(m)}n_{i,\sigma} + \frac{U^{(m)}}{2}n_{i,\sigma}n_{i,\bar{\sigma}} + t^{(m)}(c_{i,\sigma}^{\dagger}c_{i+1,\sigma} + \text{H.c.}) + \frac{d^{(m)}}{2} \right], \quad (7)$$

$$H_c^{(m)} = \sum_{\sigma} [t_1^{(m)}c_{0,\sigma}^{\dagger}c_{1,\sigma}(1-n_{0,\bar{\sigma}}) + t_2^{(m)}c_{0,\sigma}^{\dagger}c_{1,\sigma}n_{0,\bar{\sigma}} + \text{H.c.}], \quad (8)$$

where the operators in $H^{(m)}$ now refer to the block states. The presence of occupation-dependent hopping terms in $H_c^{(m)}$ is due to the nonequivalent structure of the two- and four-particle states at the edge cell. However, for the first iteration $H_c^{(m)}$ renormalizes to the structure given in Eq. (8) and preserves its form in the following iterations.

The renormalized parameters are

$$W^{(m+1)} = E_{b,\text{ads}}^{(m)} - E_{a,\text{ads}}^{(m)} - (E_b^{(m)} - E_a^{(m)}), \quad (9)$$

$$U_0^{(m+1)} = E_{c,\text{ads}}^{(m)} + E_{a,\text{ads}}^{(m)} - 2E_{b,\text{ads}}^{(m)}, \quad (10)$$

$$U^{(m+1)} = U^{(m)} + 2(E_a^{(m)} - E_b^{(m)}), \quad (11)$$

$$\mu^{(m)} = \frac{U^{(m)}}{2}, \quad (12)$$

$$D^{(m+1)} = 2d^{(m)} + D^{(m)} + E_{a,\text{ads}}^{(m)} - 2\mu^{(m)}, \quad (13)$$

$$d^{(m+1)} = 3d^{(m)} + E_a^{(m)} - 2\mu^{(m)}, \quad (14)$$

$$t_1^{(m+1)} = t^{(m)}\xi_m\xi_{1,m}, \quad (15)$$

$$t_2^{(m+1)} = t^{(m)}\xi_m\xi_{2,m}, \quad (16)$$

$$t^{(m+1)} = t^{(m)}\xi_m^2, \quad (17)$$

with

$$\xi_{1,m} = \frac{1}{\sqrt{2}} [a_1^{(m)}(b_3^{(m)} - b_2^{(m)}) - a_2^{(m)}b_9^{(m)} - a_3^{(m)}b_8^{(m)} + a_4^{(m)}b_5^{(m)} + a_5^{(m)}b_7^{(m)}, \quad (18)$$

$$\xi_{2,m} = \frac{1}{\sqrt{2}} [c_1^{(m)}(b_2^{(m)} - b_3^{(m)}) - c_2^{(m)}b_4^{(m)} + c_3^{(m)}b_6^{(m)} - c_5^{(m)}b_5^{(m)} - c_4^{(m)}b_7^{(m)}. \quad (19)$$

Here, $E_{a,\text{ads}}^{(m+1)}$ and $(a_1^{(m+1)}, \dots, a_6^{(m+1)})$ are the lowest eigenvalue and the corresponding eigenvector, respectively, of the matrix (the supraindex m was omitted for clarity, i.e., $W \equiv W^{(m)}$, $t \equiv t^{(m)}$, etc.)

$$M_0 = \begin{pmatrix} W & 0 & t & r_2 & r_1 & 0 \\ 0 & 0 & t_1 & 0 & r & r \\ t & t_1 & W & 0 & 0 & 0 \\ r_2 & 0 & 0 & 2W + U_0 & 0 & 0 \\ r_1 & r & 0 & 0 & U & 0 \\ 0 & r & 0 & 0 & 0 & U \end{pmatrix}, \quad (20)$$

where $r = \sqrt{2}t$, $r_1 = \sqrt{2}t_1$, and $r_2 = \sqrt{2}t_2$. Similarly, $E_{b,\text{ads}}^{(m+1)}$ and $(b_1^{(m+1)}, \dots, b_9^{(m+1)})$ are given by the matrix

$$M_1 = \begin{pmatrix} W & 0 & 0 & 0 & 0 & t & 0 & t & 0 \\ 0 & W & 0 & 0 & -t_2 & 0 & -t_1 & 0 & 0 \\ 0 & 0 & W & 0 & t_2 & -t & t_1 & -t & 0 \\ 0 & 0 & 0 & 2W + U_0 & t & -t_2 & 0 & 0 & 0 \\ 0 & -t_2 & t_2 & t & 2W + U_0 & 0 & 0 & 0 & 0 \\ t & 0 & -t & -t_2 & 0 & W + U & 0 & 0 & 0 \\ 0 & -t_1 & t_1 & 0 & 0 & 0 & U & 0 & -t \\ t & 0 & -t & 0 & 0 & 0 & 0 & W + U & t_1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -t & t_1 & U \end{pmatrix}. \quad (21)$$

$E_{c,ads}^{(m+1)}$ and $(c_1^{(m+1)}, \dots, c_6^{(m+1)})$ are in turn given by the matrix M_2 below, which can be obtained from M_0 by performing an electron-hole transformation:

$$M_2 = \begin{pmatrix} W+U & 0 & -t & r_1 & r_2 & 0 \\ 0 & 2W+U_0 & -t_2 & 0 & r & r \\ -t & -t_2 & W+U & 0 & 0 & 0 \\ r_1 & 0 & 0 & 2U & 0 & 0 \\ r_2 & r & 0 & 0 & U+2W+U_0 & 0 \\ 0 & r & 0 & 0 & 0 & U+2W+U_0 \end{pmatrix}. \quad (22)$$

$E_d^{(m)}$ and $E_b^{(m)}$ are, respectively, the lowest eigenvalues of matrices M_0 and M_1 for the substrate parameters $W=0$, $U_0=U$, and $t_1=t_2=t$. Equivalently, ξ_m is given by Eq. (18) where $a_i^{(m)}$ and $b_i^{(m)}$ are the corresponding eigenvectors for the substrate parameters. After a few iterations (~ 10) the renormalized hopping matrix elements vanish and we obtain the fixed-point Hamiltonian, which remains invariant at every iteration. The binding energy E_b is calculated as the difference between the total energy of the system with the adatom and that in which the adatom is decoupled from the substrate ($t'=0$). That is,

$$|E_b| = \lim_{n \rightarrow \infty} [E_n(t'=0) - E_n(t')], \quad (23)$$

where

$$E_n(t') = W^{(n)} - \mu^{(n)} + D^{(n)} \quad (24)$$

and

$$E_n(t'=0) = \left[1 - \frac{1}{3^n} \right] (d^{(n)} - \mu^{(n)}). \quad (25)$$

Note that the quantities E_n correspond to cells of 3^n atoms, therefore $D^{(n)}$ and $d^{(n)}$ are of order 3^n . This fact has to be taken into account in evaluating the limit in Eq. (23). In Eq. (25), $E_n(t'=0)$ is given by the energy of a bulk chain of $3^n - 1$ atoms (the decoupled adatom has zero energy). The charge at the adsorbed atom site is given by

$$\langle n_0 \rangle = \lim_{n \rightarrow \infty} \langle \sigma, m | n_0 | \sigma, m \rangle, \quad (26)$$

where $|\sigma, m\rangle$ is the edge-cell eigenstate corresponding to 1 particle per site at the m th iteration. The mean value $\langle v, m | n_0 | v, m \rangle$ ($v = \uparrow, \downarrow, 0, \uparrow\downarrow$) is given by the recursive formula

$$\langle v, m | n_0 | v, m \rangle = \sum_{v'} |\langle v', m-1 | v, m \rangle|^2 \times \langle v', m-1 | n_0 | v', m-1 \rangle, \quad (27)$$

where $\langle \sigma, 0 | n_0 | \sigma, 0 \rangle = 1$, $\langle \uparrow\downarrow, 0 | n_0 | \uparrow\downarrow, 0 \rangle = 2$, etc. The charge at different substrate sites are calculated in an analog manner noting that $\langle \sigma, m | n_l | \sigma, m \rangle = 1$ if $l > 3^m$: at each iteration the considered site approaches the renormalized impurity site and merges with it for $3^m \gg l$. The intermediate iterations are handled differently depending on the site considered. Formally this implies

that in Eq. (27) $|v, m\rangle$ must be replaced by a state corresponding to the direct product of a set of cells that include the considered atom, and n_0 by $n_{l(m)}$, where $l(m)$ is the index numbering the cell that contains the considered atom in the m th iteration, for example, if $l(0)=6$, then $l(1)=2$ and $l(m)=0$ for $m \geq 2$.

III. RESULTS AND DISCUSSION

In Fig. 2 we show the results obtained for the binding energy as a function of W for different values of the on-site Coulomb repulsion U_0 at the impurity site. The obtained curves are symmetric with respect to $W_0 = (U - U_0)/2$, the value for which the charge transference vanishes. In the limit $t = t' = 0$, for $W = W_0$, transferring an electron from the impurity to the chain

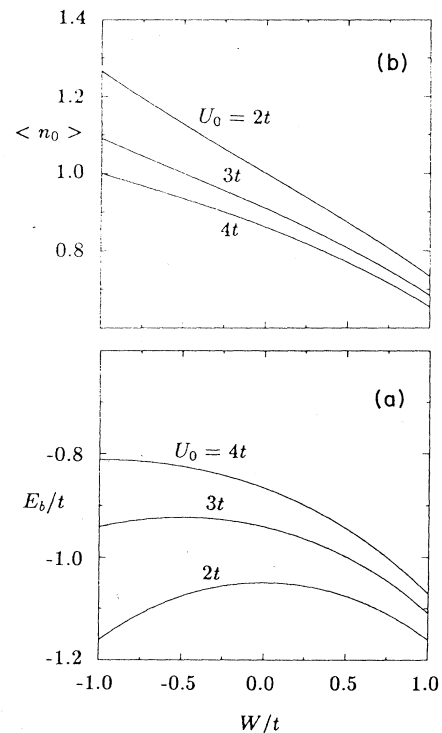


FIG. 2. (a) Binding energy and (b) impurity charge as a function of the atomic-level energy W of the adsorbed atom for $U/t=2$ and $t'/t=1.2$.

implies an energy cost that is equal to that of transferring it from the chain to the impurity. The binding energy increases with the degree of charge transference. In a perturbation expansion in t' , the binding energy E_b can be written as

$$E_b \sim -\frac{t'^2}{|U_0 + W|} - \frac{t'^2}{|U - W|}. \quad (28)$$

In Eq. (28) the first (second) term in the right-hand side represents the correction due to a virtual jump from the chain (impurity) to the impurity (chain). As can also be seen in Fig. 2(a), for a fixed U , $|E_b|$ decreases as U_0 increases because virtual jumps from the chain to the impurity are inhibited. In Fig. 3 we show the results obtained for the charge redistribution $\Delta\rho(l) = \rho(l) - 1$, where $\rho(l)$ is the charge at site l .

In choosing the range of parameters shown in Figs. 2 and 3 we had in mind the case of on-top adsorption of H on Ni. For that case we can take¹⁷ $U = 5$ eV, $t = 2.5$ eV, $t' = 3$ eV, and $U_0 \sim 8-10$ eV. For these values, our calculated binding energy varies between 2 and 3 eV for W varying between -1.2 and 2.4 eV. The experimental value¹⁸ is $E_{b,\text{expt}} \sim -2.7$ eV.

Finally we comment on the range of validity of the method. In truncating the Hilbert space we neglect states corresponding to zero, one, five, and six particles per cell. In order to obtain feasible results these must be states with higher energy than those kept. In the bulk chain this is guaranteed by taking $\mu = U/2$. In the edge cell this implies that the parameters have to satisfy that $U/2 - U_0 < W < U/2$, a range in which the impurity charge fluctuates around 1.

In summary, we presented an extension of the real-space renormalization-group technique to the case in which there is no translational invariance. We applied

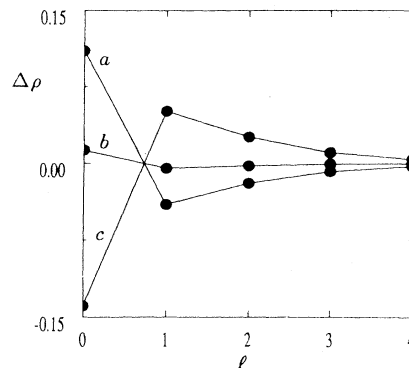


FIG. 3. Charge redistribution $\Delta\rho$ as a function of lattice site for $U/t = 2$ and $t'/t = 1.2$. Site zero corresponds to the impurity. The different curves correspond to (a) $W/t = -1.1$, $U_0/t = 3$; (b) $W/t = 1.1$, $U/t = 4$; (c) $W = 0$, $U_0/t = 4$. The continuum lines joining the dots are guides to the eye.

the method to the chemisorption problem in a Hubbard-type Hamiltonian that includes correlations in both the substrate and the adsorbed atom. The results obtained for the binding energy are close to experimental chemisorption energy values. We also calculate the charge redistribution in the first substrate sites.

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