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THE EFFECTIVE CLUSTER HAMILTONIAN FOR ADSORBED ATOMS

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Abstract. The common scheme is formulated which allows to extract the effective Hamiltonian of subsystem from the total system Hamiltonian. The non-linear equation for the effective Hamiltonian is obtained. The formalism developed is applied to describe the interaction of impurities adsorbed on the surface of the metal.

1. INTRODUCTION.

The interaction of adsorbed atoms often determines the properties of solid state surface. Two approaches are ordinarily used in theoretical study of the electron structure of the metal surface with adsorbed atoms. The first one is based on the *ab initio* (local spin density functional)

calculations and requires lengthy numerical computations. Even if the computational problems were removed, it might seem difficult to gain a simple intuitive picture of the physical mechanism involved in the phenomena under consideration.

Our paper deals with second approach presupposing the use of model Hamiltonians [1]. The calculations are essentially simplified in this case. Nevertheless a qualitative picture of the phenomenon may be still conveyed correctly. One of the most popular models in chemisorption theory was suggested by Anderson and Newns in Ref. [2]. The Anderson-Newns Hamiltonian may be written as

$$H = \sum_{k, \sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} + \sum_{\sigma} E_d d_{\sigma}^+ d_{\sigma} + \sum_{\bar{k}} (V_{k d} c_{k\sigma} d_{\sigma} + \text{h.c.}) + U n_d^{\sigma} n_d^{\sigma} \quad (1)$$

Here, d_{σ}^+ (d_{σ}) and $c_{k\sigma}^+$ ($c_{k\sigma}$) are the creation (annihilation) operators of spin σ electrons, respectively, on the adsorbed-atom and the conduction band (s-band) of substrate. Numbers E_d and ε_k are the eigenenergies of these electrons. V_{kd} denotes the hybridization potential and U describes the Coulomb repulsion of electrons on the atom adsorbed.

In the one-particle sector, the Hamiltonian (1) may be presented in the Fock space as the matrix

$$H = \begin{bmatrix} E_d & V_{k_1} & \dots & V_{k_n} \\ V_{k_1} & \varepsilon_{k_1} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ V_{k_n} & 0 & \dots & \varepsilon_{k_n} \end{bmatrix}$$

which corresponds to the basis formed by the non-perturbed one-particle states. The Anderson-Newns model may be used also to include an interaction between the atoms adsorbed.

In the present paper, we construct the effective cluster Hamiltonian which does not contain, in explicit form, the part corresponding to the conduction band of substrate. However, the interaction engendered by this band, is taken into account in

the Hamiltonian constructed. Namely, we remove from H the freedom degrees corresponding to s-electrons and keep only the adatom-electron component. Such immediate removal of the s-electron component in the spectral problem for H leads in the adatom-electron channel to the energy-dependent interactions. The latter are replaced as in Ref. [3] by the energy-independent ones. The replacement is based on solving the corresponding non-linear equation (3) for equivalent Hamiltonian of the adatom-electron channel. In fact, we illustrate our approach concerning two cases only: the case of a single impurity and the case when a cluster consists of two adsorbed atoms. At the beginning (Sect. 2) we give a short abstract description of the scheme which is applicable to arbitrary two-channel system. Then (in Sect. 3) we consider the case of a single impurity and construct the effective Hamiltonian describing one d-electron. In Sect. 4 we show that the one-particle density of states corresponding to the Hamiltonian constructed coincides with that from the Green functions method. In Sect. 5, the effective Hamiltonian is constructed for the two adsorbed atoms interacting with the conduction band.

2. THE REMOVAL OF A PART OF THE FREEDOM DEGREES.

We consider the systems with Hamiltonians allowing two-channel representation

$$H = \begin{bmatrix} h_0 & B \\ B^* & h^{in} \end{bmatrix} \quad (2)$$

Here, h_0 and h^{in} are self-adjoint operators acting in the "external", \mathcal{X} , and "internal", \mathcal{X}^{in} , channels (corresponding in our case to electrons localized respectively on the adsorbed atoms and in the conduction band of substrate electrons). Operator B , $B = \{V_{k_1}, V_{k_2}, \dots, V_{k_n}\}$, and adjoint, B^* , describe the channels coupling. Hamiltonian H acts in the sum $\mathcal{X} \oplus \mathcal{X}^{in}$ of the channel Hilbert spaces \mathcal{X} and \mathcal{X}^{in} . It is shown in Ref.[3] that

Hamiltonian H may be replaced with a more simple Hamiltonian h acting in the external channel \mathcal{X} only. Operator h is constructed in such a way that all its eigenvalues belong to the spectrum of H and corresponding eigenfunctions are the external components of the operator H eigenvectors. This means that corresponding to the external degrees of freedom, new Hamiltonian h takes into account a presence of an internal channel.

Operator equation for h reads [3] as

$$h = h_0 + W(h) \quad (3)$$

where $W(h) = B \int_{\sigma_{in}} E^{in}(d\mu) B^* (h - \mu I)^{-1}$. In this expression, σ_{in} is a

spectrum of h^{in} and $E^{in}(d\mu)$ is its spectral measure.

A solvability of eq.(3) is proved and the main properties of the operator h are listed in Ref. [3]. Here, we note only that this operator satisfies all the desired conditions. So, eq.(3) gives a way to remove the "internal" degrees of freedom corresponding to s -electrons keeping the initial adatom-electron component as an eigenfunction of a new more simple Hamiltonian.

3. A SINGLE IMPURITY.

In the case of a single impurity the d -electron channel space \mathcal{X} is one-dimensional, $\mathcal{X} = \mathbb{C}$, and $h_0, h_0 = E_d$, is a number; $h^{in} = \text{diag}\{\varepsilon_{k_1}, \varepsilon_{k_2}, \dots, \varepsilon_{k_n}\}$, $B = \{V_{k_1}, V_{k_2}, \dots, V_{k_n}\}$ and $\mathcal{X}^{in} = \mathbb{C}^n$, $n \leq \infty$. The desired Hamiltonian h is also a number satisfying eq.(3) which may be written in the form

$$h = E_d + B (hI - h^{in})^{-1} B^*.$$

Hence

$$h = E_d + \sum_{i=1}^n \frac{|V_{k_i}|^2}{h - \varepsilon_{k_i}} \quad (4)$$

Eq.(4) has $n+1$ solutions h_1, h_2, \dots, h_{n+1} which are eigenvalues of the total operator H . Eigenvector ξ_j of H corresponding to h_j , contains a pure d-state contribution which is proportional to $\langle P\xi_j, \xi_j \rangle$. Here, P is a projector on d-state. A resultant effective Hamiltonian of the d-subsystem is a weighted average

of h_j , $h_{res} = \sum_{j=1}^{n+1} c_j h_j$. The immediate calculations show that

$$c_j = \left[1 + \sum_i \frac{|V_{k_i}|^2}{(h_j - \varepsilon_{k_i})^2} \right] \quad (5)$$

The one-particle density of states of the adatom-electron subsystem reads as

$$\rho_d = \sum_j c_j \delta(x - h_j). \quad (6)$$

Coefficients c_j may be found also in another way as an expansion coefficients of the distribution $\delta(x-f(x))$,

$$c_j = \{ [x-f(x)]' \}^{-1} \Big|_{x=h_j} \quad (7)$$

where

$$f(x) = E_d + \sum_{i=1}^n |V_{k_i}|^2 / (x - \varepsilon_{k_i}).$$

So we developed a closed scheme to construct the effective subsystem Hamiltonian and the one-particle density of states.

Note that type (4) equations appear in the method of Green functions for the one-particle Green functions and in the Brillouin-Wigner perturbation theory.

4. THE DENSITY OF STATES IN THE GREEN FUNCTIONS METHOD.

To find the one-particle density of states one can use a standard technique of Green functions. For the Hamiltonian

concerned, the d-electron Green function is given by

$$g_d(\omega) = (\omega - E_d - \sigma)^{-1},$$

where the mass operator σ describes s-d interaction,

$$\sigma = \sum_k \frac{V_{dk} V_{kd}}{\omega - \varepsilon_k},$$

If a set of k is discrete then for the state density $\rho_d = -\text{Im} g_d(\omega - i0)/\pi$ we obtain the same expression (6).

If the thermodynamic limit is done then the spectrum ε_k becomes continuous and σ acquires a finite imaginary part $\Gamma = \pi |V_k|^2 \rho_s(\varepsilon_s)$. If one suggests that $\Gamma = \text{const}$ then $\rho_d = \Gamma / [(\omega - E_d - \text{Re}\sigma)^2 + \Gamma^2]$.

5. THE EFFECTIVE CLUSTER HAMILTONIAN.

Let us consider a cluster consisting of two adsorbed atoms which interact with the conduction band of the metal-adsorbent. A corresponding Hamiltonian may be written as

$$H = \begin{bmatrix} E_1 & \Omega & V_{1k_1} & \cdots & V_{1k_n} \\ \Omega^* & E_2 & V_{2k_1} & \cdots & V_{2k_n} \\ V_{k_1 1}^* & V_{k_1 2}^* & \varepsilon_{k_1} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ V_{k_n 1}^* & V_{k_n 2}^* & 0 & \cdots & \varepsilon_{k_n} \end{bmatrix}$$

Here, the matrix elements Ω and V_{ik} correspond to the direct transitions between adsorbed atoms and to transitions into the conduction band of substrate, respectively.

Following our common scheme we substitute

$$h_0 = \begin{bmatrix} E_1 & \Omega \\ \Omega^* & E_2 \end{bmatrix}, \quad B = \begin{bmatrix} V_{1k_1} & V_{1k_2} & \cdots & V_{1k_n} \\ V_{2k_1} & V_{2k_2} & \cdots & V_{2k_n} \end{bmatrix} \quad \text{and}$$

$h^{in} = \text{diag}\{\varepsilon_{k_1}, \varepsilon_{k_2}, \dots, \varepsilon_{k_n}\}$ into eq.(3) with $[W(h)]_{ij} =$

$$[B \int_{\varepsilon_{in}} E^{in} (d\mu) B^* (h - \mu I)^{-1}]_{ij} = \sum_{l=1}^n V_{ik_l} V_{jk_l}^* / (h - \varepsilon_{k_l} I). \text{ The equation for}$$

the effective Hamiltonian of impurity h reads as follows

$$h = \begin{bmatrix} E_1 & \Omega \\ \Omega^* & E_2 \end{bmatrix} + \sum_k \begin{bmatrix} |V_{1k}|^2 & V_{1k}^* V_{2k} \\ V_{2k}^* V_{1k} & |V_{2k}|^2 \end{bmatrix} (H_2 - \varepsilon_k I)^{-1} \quad (8)$$

Consider the case of two identical impurities, $E_1 = E_2 = E,$

$V_{1k} = V_{2k} = V_k.$ Taking the free cluster Hamiltonian in the form

$$h = \begin{bmatrix} e & w \\ w^* & e \end{bmatrix} \text{ we receive the following equations}$$

$$e = E + \sum_k |V_k|^2 / (e + w - \varepsilon_k)$$

$$w = \Omega + \sum_k |V_k|^2 / (e + w - \varepsilon_k)$$

for the effective values e and $w.$ If $w \in \mathbb{R}$ then $e \in \mathbb{R}$ too. Coming to the new variables $x = e + w$ and $y = e - w$ we have

$$y = E - \Omega,$$

$$x = E + \Omega + 2 \sum_k |V_k|^2 / (x - \varepsilon_k). \quad (9)$$

The solution y is an eigenvalue of the Hamiltonian h which corresponds to antisymmetric wave function and solution $x,$ to symmetric one. We see that the antisymmetric state does not hybridize with a conduction band of the metal. However the symmetric state hybridizes as in the case of isolated impurity. It is clear that eq.(9) has $n+1$ different solutions $x_j, j=1, 2, \dots, n+1,$ which correspond to $n+1$ solutions of eq.(8),

$$h_j = \frac{1}{2} \begin{bmatrix} x_j - E - \Omega & x_j - E + \Omega \\ x_j - E + \Omega & x_j - E - \Omega \end{bmatrix}. \text{ One can construct the}$$

effective cluster Hamiltonian as in a single impurity case,

$$h_{res} = \sum_{j=1}^{n+1} c_j h_j,$$
 where coefficients c_j are defined by eq.(7) with function $f(x)$ corresponding to eq.(9).

6. DISCUSSION.

We have constructed a scheme allowing to extract the effective non-energy-dependent Hamiltonian of subsystem from the total Hamiltonian of the interacting system. This scheme corresponds to transition from the priming particles to quasiparticles with an effective eigenenergy which interact between themselves but not with s-zone. It is necessary to underline the difference between these quasiparticles and quasiparticles appearing as a result of the interaction elimination, for example, with the help of canonical transformation. In the latter case, the quasiparticles are formed by the particles of the system considered as well as by those of the subsystem eliminated. In our case, the quasiparticles are formed by the particles of the subsystem considered only but the interaction between them turns out new. Such quasiparticle description differs from traditional one and may be useful, for example, in construction of the theory of physical adsorption and chemisorption.

Note that the problem concerned of subsystem extraction from the total system arises in a lot of physical problems. In dilute alloy theory one can consider as a subsystem, the cluster of impurities. In theory of multilayers and magnetic superlattices, such subsystem may consist of the atoms on the interface surface. This question arises also in scattering theory for particles with non-trivial internal (for example, quark) structure in connection with the problem of using two-body energy-dependent potentials in few-body calculations (see [4] and Refs. therein) that induced initially the approach [3].

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