

The decoupling problem in chemisorption of a multiple-orbital atom

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 3145

(<http://iopscience.iop.org/0953-8984/1/19/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 94.79.44.176

The article was downloaded on 10/05/2010 at 18:10

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

The decoupling problem in chemisorption of a multiple-orbital atom

Liu Zhenpeng

Department of Physics, Liaoning University, Shenyang, People's Republic of China

Received 19 September 1988, in final form 7 March 1989

Abstract. A general method for the elimination of the coupling between the d-orbital electrons of a transition-metal adatom with the surface of the substrate is presented. The result shows that all the d-orbital states have been decoupled except one even for the case where the original coupling parameters are different.

In our previous papers [1, 2], we have reduced the number of coupling d-orbital states of an adatom interacting with the substrate to only one, by using the unitary transformation. However, in those papers we assumed that all interactions between different d-orbital states of the adatom and the states of the nearest-neighbour surface atoms of the substrate take the same coupling parameter V_0 . In this Letter, therefore, the purpose is to present a general decoupling method that does not require this restriction.

In the Anderson–Newns model, the Hamiltonian of the multiple-orbital atom chemisorption problem can be written as

$$H = E_d \sum_{m\sigma} n_{m\sigma} + \frac{1}{2}U \sum_{m'\sigma' \neq m\sigma} n_{m\sigma} n_{m'\sigma'} + H^s + \sum_{m\sigma} V_m (C_{m\sigma} Q_\sigma + \text{HC}) \quad (1)$$

where m and σ label the ten degenerate d orbitals of spin σ and energy E_d . $n_{m\sigma} = C_{m\sigma}^+ C_{m\sigma}$ is the number operator of the $|m\sigma\rangle$ orbital, Q_σ denotes the substrate part of the operators which couples with that of the adatom. In general, Q_σ consists of creation operators in the Wannier representation at the nearest-neighbour sites of the adatom. The number of the sites depends on the types of the adatom binding [3]. U is the interatomic Coulomb repulsion between the electrons localised in the d orbitals of the adatom. The term H^s is a tight-binding Hamiltonian of the semi-infinite substrate, and the coefficients V_m are the coupling parameters between $|m, \sigma\rangle$ orbitals with the substrate surface. In a previous paper [1] we pointed out that, except for the last term, all the terms in (1) are invariant under the unitary transformation for the adatom operators. Hence we will only pay attention to the last term of (1), which is (hereafter, we omit the spin subscript)

$$H_1 = \sum_m V_m C_m Q + \text{HC}. \quad (2)$$

For any two operators C_i and C_j , we can find the following unitary transformation

$$\begin{pmatrix} C_i \\ C_j \end{pmatrix} = (V_i^2 + V_j^2)^{-1/2} \begin{pmatrix} V_j & V_i \\ -V_i & V_j \end{pmatrix} \begin{pmatrix} a_i \\ a_j \end{pmatrix}. \quad (3)$$

Using (3) in (2) gives

$$(V_i C_i + V_j C_j)Q = (V_i^2 + V_j^2)^{1/2} a_j Q. \quad (4)$$

This has reduced the number of coupling operators by one. Thus, we can perform a similar procedure four times, and finally the result becomes

$$H_1 = \left(\sum_m V_m^2 \right)^{1/2} a_5 Q + \text{HC}. \quad (5)$$

At the same time the solitary remaining coupling state is

$$a_5^\dagger |0\rangle = \left(\sum_m V_m^2 \right)^{-1/2} \left(\sum_m V_m C_m^\dagger \right) |0\rangle. \quad (6)$$

In fact we can combine the four sequential procedures into one, namely

$$\begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \end{bmatrix} = \begin{bmatrix} V_1 V_2 [1 \ 2] & V_1 V_3 [2 \ 3] & \cdot & V_1 V_5 [4 \ 5] & V_1 [5]^{-1/2} \\ -[1] [1 \ 2] & V_2 V_3 [2 \ 3] & \cdot & V_2 V_5 [4 \ 5] & V_2 [5]^{-1/2} \\ 0 & -[2] [2 \ 3] & \cdot & V_3 V_5 [4 \ 5] & V_3 [5]^{-1/2} \\ 0 & 0 & \cdot & V_4 V_5 [4 \ 5] & V_4 [5]^{-1/2} \\ 0 & 0 & 0 & -[4] [4 \ 5] & V_5 [5]^{-1/2} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \end{bmatrix} \quad (7)$$

where

$$[N] = \sum_{m=1}^N V_m^2 \quad [N \ M] = \left[\left(\sum_{i=1}^N V_i^2 \right) \left(\sum_{j=1}^M V_j^2 \right) \right]^{-1/2}. \quad (8)$$

When all the $V_m = V_0$, the expressions (5) and (6) are reduced to

$$H_1 = \sqrt{5} V_0 (a_5 Q + \text{HC}) \quad (5')$$

$$a_5^\dagger |0\rangle = 1/\sqrt{5} \left(\sum_{m=1}^5 C_m^\dagger \right) |0\rangle \quad (6')$$

which is in agreement with the result of our previous paper [1]. In the single adatom case, the problem has axial symmetry. If $m = 1, 2, 3, 4, 5$ corresponding to the magnetic quantum number $1, -1; 2, -2; 0$, respectively, then we get $V_1 = V_2, V_3 = V_4$. If the interaction depends only on the parity under the surface reflection, then besides $V_1 = V_2, V_3 = V_4$, we have $V_3 = V_4 = V_5$.

In summary, no matter how different the original coupling parameters of the problem are, they can always be reduced to only one. It means that the main qualitative conclusions of our previous papers [1, 2] are still unchanged. It should be pointed out that a similar procedure, which redefined substrate states as being orthogonal to the selected linear combination of those which coupled to the adatom, has been widely used in chemisorption theory to decouple degenerate substrate modes [4–6]. Of course, there is a limitation in applying the decoupling procedure, which also may be a rather artificial property of the Anderson–Newns model, which is that the degeneracy of the adorbitals is not lifted by the substrate field.

References

- [1] Liu Zhenpeng 1987 *J. Phys. C: Solid State Phys.* **20** 5485
 [2] Liu Zhenpeng 1988 *Acta Phys. Sin.* **37** 1814

- [3] Einstein T L and Schrieffer J R 1973 *Phys. Rev. B* **7** 3629
- [4] Delanaye *et al* 1978 *Surf. Sci.* **70** 629
- [5] Doyen G 1976 *Surf. Sci.* **59** 461
- [6] Doyen G and Grimley T B 1978 *Photoemission and the Electronic Properties of Surfaces* ed. B Feuerbacher *et al* (Chichester: Wiley) p 137