Surface phenomenon of chemisorption and its effect on density of states with reference to correlation on the metal surface

S Patra
Department of Physics, G B Pant University of Agriculture & Technology, Pantnagar 263145

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A change in density of states is obtained by inclusion of intra-atomic interaction term to the mixing Hamiltonian constructed due to chemisorbed adatoms with the clean metal surface. The double-time Green function technique was employed in the Zubarev’s equation of motion formalism and in order to decouple the hierarchy of higher order Green functions Hartee-Fock decoupling approximation was assumed. From the corresponding surface Green function, the modified density of states was obtained through which chemisorption energy and energy of localization were estimated and it was found that they were of the same order as per the prediction.

Keywords: Chemisorption, Density of states, Green function

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1 Introduction

The theory of chemisorption by several researchers1,2 has been developed to study the surface properties3 of metals and alloys. The molecular orbital approach and the valence band approach are found to be much more emphasized. Introduced by Schriffer and Gomer4 and later on developed by Paulson and Schriffer5, the latter theory although gives importance to ionic configuration but ignores correlation effect. In most of these previous calculations for the surface parameters, a significant deviation is sometimes observed between the experimental result and theoretical predictions perhaps due to the neglect of correlation due to intra-atomic interaction between the chemisorbed atoms in the clean metal surface and dilute alloys.

2 Model Hamiltonian

To investigate the physical parameters, the model Hamiltonian, guided by the above criteria and experimental data, can be considered as follows:

\[ H = H_{\text{mol}} + H_{\text{ind}} + V + W \]  \hspace{1cm} \text{... (1)}

where \( H_{\text{mol}} \) is the surface molecular part representing chemisorption part; \( H_{\text{ind}} \) is the indented solid part representing substrate molecular part; \( V \) is the inter-atomic Coulomb repulsion part and \( W \) is the intra-atomic interaction part.

Among the existing theoretical techniques, the methods of Zubarev double-time Green’s function6-8, local density functional (LDF) formalism and Feynman Diagram Technique are the powerful mathematical tools of the Quantum Field theoretical models within Hamiltonian approach. The former methodology determines the excitation spectrum through its analytic properties in the complex energy plane and consequently leads to general expression for experimentally measured quantities such as electrical conductivities and magnetic susceptibilities. Further, another important property of the above method is that the Green’s functions are related, via the fluctuation-dissipation theorem to time correlation functions which determine the average needed to discuss properties of the ground state of the system. In view of above in the present work to investigate the superconducting parameters like transition temperature \((T_C)\) and order parameter \((\Delta)\), we follow the double-time Green’s function method, which can be briefly summarized as follows:

The double-time temperature dependent retarded (+) and advance (–) Green’s function involving two parameters \( A \) and \( B \) are defined by:

\[ \langle\langle A(t)|B(t')\rangle\rangle^{(\pm)} = \pm i0[\pm(t-t')]\langle[A(t),B(t')]\rangle_\eta > \]  \hspace{1cm} \text{... (2)}

where,

\[ [A,B]_\eta = AB - \eta BA \]

\[ \eta = +1 \text{ for bosons} \]
\[ \eta = -1 \text{ for fermions and} \]

\[ A(t) = e^{iHt}A(0)e^{-iHt} \]
\( \theta(t) \) is the unit step function, unity for positive \( t \) and zero for negative \( t \), and the notation \( \langle \cdots \rangle \) denotes an average over a grand canonical ensemble at temperature \( T \). We assume \( \hbar = 1 \). In practice, it is convenient to work with the Fourier transform of the Green’s function with respect to:

\[
\langle A(t) B(t') \rangle_{\omega_0} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle A(t) B(t') \rangle_{\omega_0} e^{i\omega(t-t')} d(t-t') \]

... (3)

The Fourier transform satisfies the equation of motion:

\[
\omega \langle A(t) B(t') \rangle_{\omega_0} = \frac{1}{2\pi} \langle [A,B]_{\omega_0} \rangle_{\omega_0} + \langle [A,H] B(t') \rangle_{\omega_0} \]

... (4)

where \( \langle A(t) B(t') \rangle_{\omega_0} = \langle A(t) B(t') \rangle_{\omega_0}^{(+)} \) if \( \text{Im} \omega > 0 \)

\( = \langle A(t) B(t') \rangle_{\omega_0}^{(-)} \) if \( \text{Im} \omega < 0 \) ... (5)

Further, it can be shown that the correlation function \( \langle B(t') A(t) \rangle \) is related to the Green’s function which is given by:

\[
\langle B(t') A(t) \rangle = \lim_{e \to 0} \int_{-\infty}^{\infty} \left[ \frac{\langle A(t) B(t') \rangle_{\omega + i\epsilon} - \langle A(t) B(t') \rangle_{\omega - i\epsilon}}{e^{i\eta} - 1} \right] e^{i\omega(t-t')} d\omega \]

... (6)

where, \( \beta = 1/k_B T \) and \( k_B \) is the Boltzmann constant. In our analysis, as per example, to obtain the self-consistent expression for transition temperature \( (T_C) \) and order parameter \( (\Delta) \) as a function of hybridization \( (V) \), when we set-up an equation of motion for the corresponding Green’s function by using Zubarev formula, higher order Green’s functions will appear and the system of equations does not close. One can in turn write down the equations of motion of the new Green’s functions, thus obtaining Green’s functions of still higher order. To truncate the infinite hierarchy of differential equations, one can use suitable decoupling approximations which reduce higher order Green’s function to lower order Green’s function and help in solving them to obtain expressions for required experimental parameters.

### 3 Calculation and Results

We defined the three types of surface Green functions in accordance with:

\[
G_{AA}(E) = \langle < C_{\alpha \sigma} / C_{\alpha \sigma} > \rangle \]

... (7)

Which may be subsequently expressed as follows:

\[
G_{11}(E) = \langle < C_{1 \sigma} / C_{1 \sigma} > \rangle \]

... (8)

\[
G_{22}(E) = \langle < C_{2 \sigma} / C_{2 \sigma} > \rangle \]

... (9)

and \( G_{12}(E) = \langle < C_{1 \sigma} / C_{2 \sigma} > \rangle \)

... (10)

where \( C_{1 \sigma}^+, C_{2 \sigma}^+ \) are Creation operators and \( C_1 \) and \( C_2 \) are the annihilation operators for the site 1 and site 2 of different chemisorbed atoms respectively analogous to electronic states \(|1>\) and \(|2>\).
We employed the Zubarev equation of motion and in order to decouple the hierarchy of higher order Green functions assumed Hartee-Fork approximation and obtained the expressions of the three surface Green functions and hence obtained the density of states by calculating the imaginary part of the corresponding Green functions which is related through the following formula as example:

$$\rho_{11}(E) = \frac{1}{\pi} \text{Im} G_{11}(E) \quad \ldots (11)$$

and it is based on the fact that the eigen states of the indented solid are the solutions of the scattering problem for an electron (atom) plus the semi-infinite solid with the indent at the site 1 and 2, respectively.

Thus, the density of states (modified) $\rho'(E)$ due to correlation is estimated by taking the concerned Green functions and compared with the $\rho_{\text{effect}}(E)$ and $\rho_{11}(E)$ and found that it was in between the semi-elliptic value in curve of $\rho_{\text{effect}}(E)$ and that of $\rho_{11}(E)$ (see Fig. 1).

After obtaining the modified DOS, the localized energy and chemisorption energy were calculated using the following standard expressions i.e.

**Case I—For localized energy**

$$E_{\text{loc}} = E_F - E_{F_\text{m}} + 2 \int_{-\infty}^{\infty} (E - E_F) \rho'(E) dE \quad \ldots (12)$$

where

(i) $\Delta \rho'(E) = \frac{1}{\pi} \text{Im} \frac{\partial}{\partial E} G_{12}(E) + \frac{1}{4} U_1 n_1^2$

(ii) $G_{12} = \left[ \left( G_{12}(E) \right)^{-1} - \frac{1}{2} U_1 n_1 \right]^{-1}$

and (iii) $G_{12}(E) = E - E_{F_1} - T^2 \sum_q \frac{A_q^2}{E - E_q}$

**Case II—For chemisorption energy (Ref. 9)**

$$\Delta E = \int_{-\infty}^{\infty} \rho'(E) E dE - E_F - U n_1^2 \quad \ldots (13)$$

where the terms used in defining the expression given in Eq.(13) have their usual meaning as follows:
(i) \( \rho'(E) \) represents changed density of states; (ii) \( U_i \) represents intra-atomic interaction of the atom \( |1\rangle \); (iii) \( n_1 \) represents the average number of electron in the atom \( |1\rangle \); (iv) \( A_q \) represents \( \sum_{i=1}^{NN} \langle i/q \rangle \) where, \( \sum_{i=1}^{NN} \) represents the sum over the nearest neighbours of the atom \( |1\rangle \); (v) \( T \) represents hoping term connected with the bandwidth \( W_B \) by \( W_B = 12 T \); (vi) \( \epsilon_1 \) represents free energy of the atom \( |1\rangle \); (vii) \( \epsilon_F \) represents Fermi energy related to free energy of the atom \( |1\rangle \) as \( \epsilon_F = \epsilon_1 + \frac{1}{2} + \omega/2 \); (viii) \( \epsilon_q \) represents free energy of the substrate atom; (ix) \( E_{\text{loc}} \) represents localization energy of the concerned orbital atom; (x) \( \Delta E_{\text{mol}} \) represents Binding energy of the surface molecule and (xi) \( E \) represents the variable energy on which various energy parameters depend on.

### 4 Results and Discussion

By comparing the localized energy i.e. the energy required to localize an electron in the orbital \( |1\rangle \) state on the clean surface with the corresponding chemisorption energy, it was found that the localized energy is of the same order or sometimes have higher value than chemisorption energy which suggests that modified density of states due to correlation may also be treated as a useful parameter to investigate the other surface properties of metals and alloys.

Also to test the validity of inclusion of intra-atomic interaction part to the model Hamiltonian, we took a mediator parameter \( E_{\text{mol}} \) to compare the chemisorption energy and localization energy of the concerned orbital (assuming standard values of the various parameters involved) graphically (see Fig. 2) which reveals that keeping the relation \( \Delta E < E_{\text{mol}} \) intact \( \Delta E'_{\text{mol}} \) diverges more and more after attaining absolute minimum value in the present case whose effects are to be pronounced more and more relevant in comparison to the respective experimental values\(^{10}\), suggesting its usefulness in modification of the surface parameters of metals and dilute alloys.

### References