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Electron-phonon interaction in the surface dimer adsorption model

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In the scope of the model of surface dimer, formed by the adsorbed atom and below lying substrate surface atom, the problem on the electron-phonon interaction effect on the charge transfer in adsorbed system is considered. The case of adsorption on metal is examined thor oughly.

Keywords: adsorbate, substrate, dimer's vibrations, charge transfer.

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1. Introduction

To the best of the authors' knowledge, the question of the adatom vibrations effect on its electronic state was first considered in articles [1–3]. In this case, the adsorption standard model (ASM) was used on Anderson–Newns metals [4,5]. Recently, to describe adsorption on solid substrates, the surface dimer model (SDM) was proposed, which, unlike the standard model, considers not an adsorbed particle, but a surface molecule formed by this particle and the nearest atom of the substrate surface [6]. In this article, we consider how vibrations of a surface dimer affect the electronic characteristics of an adsorption system and, most importantly, charge transfer within a dimer and between a dimer and a substrate. Although in the case under consideration it is more correct to speak of electron-vibrational interaction, we will use the standard term „electron-phonon" interaction, comparing the eigenfrequency of Ω dimer vibrations with a phonon with a zero wave vector.

Let us represent the Hamiltonian of a free (not bound to the substrate) dimer H_{dim}, consisting of atoms a (adsorbed atom) and s (surface atom of the substrate), which orbitals are characterized by energies ε_a and ε_s, and the occupation numbers are 1, as the sum of $H_{\text{dim}} = H_{el} + H_{vib} + H_{\text{int}}$. The Hamiltonian of the subsystem of spinless electrons has the form

$$H_{el} = \varepsilon_a \hat{n}_a + \varepsilon_s \hat{n}_s - t(s^+ a + a^+ s), \tag{1}$$

where t is energy of electron hopping between atoms a and s, $\hat{n}_a = a^+ a$ and $\hat{n}_s = s^+ s$ are atomic number operators for a and s, $a^+(a)$ and $s^+(s)$ are electron creation (annihilation) operators, $n_{s(a)}$ are atomic occupation numbers a and s [6]. The Hamiltonian H_{vib} describing the vibrations of a free surface dimer can be represented in the classical form

$$H_{vib} = \frac{1}{2} M \dot{l}^2 + \frac{1}{2} k (l - l_0)^2, \tag{2}$$

where M is reduced mass of dimer atoms, $k = M\Omega^2$ is force constant of dimer with equilibrium length l_0. The Hamiltonian of the interaction H_{int} between the electronic and vibrational subsystems of a free dimer is

$$H_{\text{int}} = \nu (\hat{n}_a + \hat{n}_s)(l - l_0), \tag{3}$$

where ν is deformation constant of the surface dimer. Using the relation $\partial \langle H_{\text{dim}} \rangle / \partial l = \langle \partial H_{\text{dim}} / \partial l \rangle$, we get $l - l_0 = -\nu (n_a + n_s)/k$. Then the Hamiltonian H_{dim} can be written as

$$H_{\text{dim}} = w_a \hat{n}_a + w_s \hat{n}_s - t(s^+ a + a^+ s) + H'. \tag{4}$$

Here $w_{a(s)} = \varepsilon_{a(s)} - \lambda n_{a(s)}$, where $\lambda = \nu^2/k$ is the constant of the electron-phonon interaction of the surface dimer and the term H' contains all the contributions that do not have an operator structure. Using the results of [6] and neglecting the metallicity of the bond, we obtain

$$\nu = (\partial \sqrt{t^2 + \delta^2} / \partial l)_{l = l_0} = 4 t \alpha_c / l_0,$$

$$k = 4 \alpha_c t (1 - 2\alpha_p^2)/l_0^2 \quad \text{and} \quad \lambda = 4 \alpha_c t / (1 - 2\alpha_p^2),$$

where bond covalency $\alpha_c = t/\sqrt{t^2 + \delta^2}$, bond polarity $\alpha_p = \sqrt{1 - \alpha_c^2}$ and $\delta = (\varepsilon_a - \varepsilon_s)/2$ [7].

Hamiltonian (4) corresponds to the Green's function of the free dimer $g^{\pm}_{\text{dim}}(\omega) = (\omega - \omega_{\pm} + i0^+)^{-1}$, where ω is energy variable and energies of local levels are $\omega_{\pm} = w \pm R$, $R = \sqrt{\Delta^2 + t^2}$, $w = (w_a + w_s)/2$ and $\Delta = (w_a - w_s)/2$. The densities of atom states of a free dimer are

$$\rho_{a,s}(\omega) = D_{\pm} \delta(\omega - \omega_+) + D_{\mp} \delta(\omega - \omega_-),$$

where $D_{\pm} = (1 \pm \Delta/R)/2$ (upper signs refer to atom a, lower refer to atom s), $\delta(\ldots)$ is Dirac delta function. The state density of the free dimer itself is $\rho_{\text{dim}}(\omega) = \delta(\omega - \omega_+) + \delta(\omega - \omega_-)$, and the occupation number $n_{\text{dim}} = 2[\Theta(\omega - \omega_+) + \Theta(\omega - \omega_-)]$, where $\Theta(\ldots)$ is Heaviside function. Then, we set $\varepsilon_a + \varepsilon_s - 2\lambda = 0$, where we take into account that $n_a + n_s = 2$ in a free dimer. The charge transfer between atoms of a free dimer is $m = n_a - n_s$, so $\Delta = \delta - \lambda m/2$, where $\delta = (\varepsilon_a - \varepsilon_s)/2$. It is easy to show that $\partial m/\partial\lambda = -mt^2/R^3$, i.e. as λ increases, the value of $|m|$ decreases.

Let's take into account the presence of a substrate. In the weak coupling limit ($\Gamma(\omega) \ll t$), dencity of states of thr epitaxial dimer densities of the epitaxial dimer (epidimer) $\bar{\rho}_{\text{dim}}(\omega)$ and its constituent atoms $\bar{\rho}_{a(s)}(\omega)$ can be represented as

$$\bar{\rho}_{a(s)}(\omega) = D_{\pm}\rho_+(\omega) + D_{\mp}\rho_-(\omega),$$

$$\bar{\rho}_{\text{dim}}(\omega) = \rho_+(\omega) + \rho_-(\omega),$$

$$\rho_{\pm}(\omega) = \frac{1}{\pi}\,\frac{\Gamma(\omega)}{(\omega - \omega_{\pm} - \Lambda(\omega))^2 + \Gamma^2(\omega)}. \qquad (5)$$

Here $\Gamma(\omega) = \pi V^2 \rho_{\text{sub}}(\omega)$ is the local level broadening function $\omega_{\pm}$, the function

$$\Lambda(\omega) = V^2 P \int\limits_{-\infty}^{\infty} \rho_{\text{sub}}(\omega')(\omega - \omega')d\omega'$$

determines the shift of these levels, $\rho_{\text{sub}}(\omega)$ is density of substrate states, V is matrix element of the interaction of $\omega_{\pm}$ levels with substrate states, P is principal value symbol. For further analysis, it is necessary to specify the substrate by setting the function $\rho_{\text{sub}}(\omega)$.

Let us consider adsorption on metal. Setting $\rho_{\text{sub}}(\omega) = \rho_m = \text{const}$ (Anderson model [5]), we find $\Gamma(\omega) = \Gamma_m = \pi V^2 \rho_m$ and $\Lambda(\omega) = \Lambda_m = 0$. Then the densities of states of the epidimer atoms $\bar{\rho}^m_{a(s)}(\omega)$ are the sums of two Lorentz profiles $\rho^m_{\pm}(\omega) = \Gamma_m/\pi[(\omega - \omega_{\pm})^2 + \Gamma_m^2]$ with weight factors $D_{\pm}$ [6,7]. At zero temperature, the level occupation numbers $\omega_{\pm}$ are equal to

$$n^m_{\pm} = 2\int\limits_{-\infty}^{\varepsilon_F} \rho^m_{\pm}(\omega)d\omega,$$

where ε_F is the Fermi level of the system, whence, taking into account (5), we find $n^m_{\pm} = (2/\pi)\text{arccot}[(\omega_{\pm} - \varepsilon_F)/\Gamma_m]$. For the epidimer, the occupation number is

$$\bar{n}^m_{\text{dim}} = n^m_+ + n^m_- \quad \text{and} \quad \bar{m}^m \equiv \bar{n}^m_a - \bar{n}^m_s = (\bar{\Delta}/\bar{R})(n^m_+ - n^m_-),$$

where $\bar{\Delta} = \delta - \lambda\bar{m}^m/2$, $\bar{R} = \sqrt{\bar{\Delta}^2 + t^2}$. At $\varepsilon_F = 0$ there is no charge transfer between the dimer and the substrate, so $\bar{n}^m_{\text{dim}} = 2$. The interatomic charge transfer inside the dimer is

$$\bar{m}^m = (2\bar{\Delta}/\pi\bar{R})\big[\arctan(\omega_-/\Gamma_m) - \arctan(\omega_+/\Gamma_m)\big].$$

In the weak coupling regime, the dimer-substrate $\Gamma_m/|\omega_{\pm}| \ll 1$ and $\Gamma_m/R \ll 1$ in the first approximation, we have

$$n^m_+(\varepsilon_F = 0) \approx 2\Gamma_m/\pi\omega_+ \text{ and } n^m_-(\varepsilon_F = 0) \approx 2 - 2\Gamma_m/\pi\omega_-.$$

Therefore,

$$(\bar{m}^m)_{\varepsilon_F = 0} \approx -2(\bar{\Delta}/\bar{R})(1 - 2\Gamma_m/\pi\bar{R}).$$

Thus, at $\varepsilon_F = 0$, the value of the interatomic charge transfer in the epidemer is smaller than in the free dimer. In the limit $|\varepsilon_F| \ll |\omega_{\pm}|$ we have $n^m_{\pm} \approx n^m_{\pm}(\varepsilon_F = 0) - 2\rho^m_{\pm}(\omega_{\pm})\varepsilon_F$, where $\rho^m_{\pm}(\omega_{\pm})\varepsilon_F \sim \Gamma_m\varepsilon_F/\bar{R}^2$, i.e. it is a quantity of the second order infinitesimal. In the same limit, the charge transfer between the dimer and the substrate is $\bar{m}^m_{\text{dim}} = 2 - \bar{n}^m_{\text{dim}} \approx 2\Gamma_m/\bar{R}$, or a quantity of the first order infinitesimal. At the same time $\partial\bar{m}^m_{\text{dim}}/\partial\lambda = (\Gamma_m\bar{\Delta}/\bar{R}^3)\bar{m}^m_{\text{dim}}$, so that the electron-phonon interaction increases the value of $|\bar{m}^m_{\text{dim}}|$ at $\bar{\Delta} > 0$ and decreases it at $\bar{\Delta} < 0$.

Above, we considered the case of a weak bond between the dimer and the substrate. It is easy to show (e.g. see [8]) that in the strong bond regime in the zeroth order in t^2/Γ_m^2 the problem of epidimer is reduced to the problem of adsorption of two isolated atoms a and s. If, as in the article [8], we take into account the Coulomb repulsion G of electrons of atoms a and s, then expression (4) will be valid after replacing $w_{a(s)} = \varepsilon_{a(s)} - \lambda n_{a(s)}$ with $w'_{a(s)} = \varepsilon_{a(s)} + Gn'_{s,a} - \lambda n'_{a(s)}$.

In this article, we considered adsorption on a metal with a constant state density (Anderson model), which is applicable to the description of simple (non-transitional) metals with a wide *sp*-band. For d- and f-metals, it is more correct to use the Friedel state density model of „pedestal" type [9], shift function $\Lambda(\omega)$ for which is given in [10]. Note that the Friedel model is also suitable for describing two-dimensional metals [11]. In case of adsorption on semiconductor and dielectric substrates, it is convenient to use the Haldane–Anderson state density model [5,12]. Adsorption on graphene-like compounds is considered in [13].

Unfortunately, it should be noted that the question of the role of the electron-phonon interaction in adsorption has not been practically studied (e.g. see [4,14]), although, on the other hand, there is growing interest in electron-phonon effects in epitaxial [15,16] and free [17–19] two-dimensional layers and topological insulators [20,21]. Therefore, in the adsorption problem, due to the lack of information, we used the simplest model of electron-phonon interaction, similar to the widely used one-phonon Holstein model [22,23].

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] F.D.M. Haldane. Phys. Rev. B **13**, 281 (1977).
[2] V.E. Kravtsov, A.G. Malshukov. Tech. Phys. Lett. **44**, 105 (2018).
[3] S.Yu. Davydov. Tech. Phys. Lett. **44**, 105 (2018).
[4] S.G. Davison, K.W. Sulston. Green-Function Theory of Chemisorption. Springer, Berlin (2006). 211 p.

[5] S.Yu. Davydov, S.V. Troshin. Phys. Solid State **49**, 1583 (2007).
[6] S.Yu. Davydov, A.V. Zubov, A.A. Lebedev. Tech. Phys. Lett. **45**, 461 (2019).
[7] S.Yu. Davydov, O.V. Posrednik. Phys. Solid State **57**, 837 (2015).
[8] S.Yu. Davydov, A.V. Zubov, A.A. Lebedev. Tech. Phys. Lett. **45**, 934 (2019).
[9] V.Yu. Irkhin, Yu.P. Irkhin. Elektronnaya struktura, fizicheskiye svoystva i korrelyatsionnyye effekty v d- i f-metallakh i ikh soyedineniyakh UrO RAN, Ekaterinburg (2004). 472 p. (in Russian).
[10] S.Yu. Davydov, O.V. Posrednik. Tech. Phys. Lett. **47**, 566 (2021).
[11] S.Yu. Davydov, O.V. Posrednik. Semiconductors **55**, 782 (2021).
[12] F.D.M. Haldane, P.W. Anderson. Phys. Rev. B **13**, 2553 (1976).
[13] S.Yu. Davydov. Semiconductors **51**, 217 (2017).
[14] Ph. Hofmann, I.Yu. Sklyadneva, E.D.L. Rienks, E.V. Chulkov. New J. Phys. **11**, 125005 (2009).
[15] M. Bianchi, E.D.L. Rienks, S. Lizzit, A. Baraldi, R. Balog, L. Hornekær, Ph. Hofmann. Phys. Rev. B **81**, 041403(R) (2010).
[16] G. Benedek, J.R. Manson, S. Miret-Artés. Chem. Phys. Phys. Chem. **23**, 7575 (2021).
[17] N. Nayyar, D. Le, V. Turkowski, T.S. Rahman. arXiv: 1501.07908.
[18] F. Karsai, M. Humer, E. Flage-Larsen, P. Blaha, G. Kresse. Phys. Rev. B **98**, 234205 (2018).
[19] L. Chen, O. Skibitzki, L. Pedesseau, A. Létoublon, J. Stervinou, R. Bernard, C. Levallois, R. Piron, M. Perrin, M.A. Schubert, A. Moréac, O. Durand, T. Schroeder, N. Bertru, J. Even, Y. Léger, C. Cornet. ACS Nano **14**, 13127 (2020).
[20] R. Heid, I.Yu. Sklyadneva, E.V. Chulkov. Sci. Rep. **7**, 1095 (2016).
[21] J. Zhu, Y. Xia, G. Li, S. Zhou, S. Wimmer, G. Springholz, A. Pashkin, M. Helm, H. Schneider. Appl. Phys. Lett. **114**, 162105 (2019).
[22] T. Stauber, N.M.R. Peres. J. Phys.: Condens. Matter **20**, 055002 (2008).
[23] N. Sakkinen, Y. Peng, H. Appel, R. van Leeuwen. J. Chem. Phys. **143**, 234102 (2015).

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