MOTION AND STICKING OF QUANTUM PARTICLES NEAR POLARIZABLE SURFACES. MODEL CALCULATIONS

Ž. Crljen[*] and B. Gumhalter[**]

[*]"R. Bošković" Institute and [**]Institute of Physics of the University, 41001 Zagreb, Yugoslavia

Abstract

The effects of reactive and dissipative forces on the motion and inelastic scattering of quantum particles near metallic surfaces and their consequences on adsorption and similar phenomena are examined within the framework of the surface response of the substrate Fermi sea.

1. Introduction

When a thermalized neutral particle (atom or molecule) approaches a metallic surface, it experiences first a potential due to the electronic and ionic polarization of the substrate. The reactive and dissipative components of this potential will strongly affect the particle motion in the close vicinity of the surface, up to the point where the metallic and adparticle electronic wavefunctions start to overlap. Depending on the orbital structures of both the adparticle and the metal, the overlap effects may give rise to additional interactions which may then lead to the formation of a chemical bond between the adsorbate and the substrate. In order to make the adsorption possible, the interaction of the particle with the substrate must provide a reactive potential with a minimum near the surface and also a dissipative component by means of which the particle could lose its energy to the substrate degrees of freedom. In this report we present a brief account of a part of our study in which we deal with the case where the adparticle motion is not appreciably affected by the overlap effects. This model describes, for instance, a very important dissipation mechanism in physisorption and also the starting process in activated chemisorption in which the particle adsorbs via a precursor state.

2. Formulation of the Model

A rather general formulation of the adatom interaction with a metal starts from the following Hamiltonian:

$$\mathcal{H} = \frac{\vec{P}^2}{2M} + \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_i \int d^3r' \frac{e\, q(\vec{r}\,')}{|\vec{r}_i - \vec{r}\,'|} , \qquad (1)$$

where $\vec{P}$, M and $q(\vec{r}\,')$ are the particle momentum, mass and charge density distribution, respectively, and $\vec{p}_i$, m, e and $\vec{r}_i$ denote the momentum, mass, charge and position of the substrate electrons, respectively, which occupy the halfspace $z<0$. In view of a rather weak initial interaction between the adparticle and the substrate, we proceed by making use of the quantum counterpart of the image theorem /1/ and reformulate the problem in terms of the linear response /2/. This enables us to construct an equivalent Hamiltonian as regards the adparticle-substrate interaction:

$$H = \frac{\vec{P}^2}{2M} + \sum_{\vec{Q}} \int_0^\infty d\omega \omega N_Q(\omega) \left(a^+_{\vec{Q}\omega} a_{\vec{Q}\omega} + \frac{1}{2}\right) +$$

$$+ \sum_{\vec{Q}} e^{i\vec{Q}\vec{\rho}} \int_0^\infty d\omega N_Q(\omega) \sqrt{\omega U_Q(-z)/2} \left(a_{\vec{Q}\omega} + a^+_{-\vec{Q}\omega}\right) . \qquad (2)$$

Here $\vec{r}=(\vec{\rho},z)$ is the radiusvector of the adparticle centre of mass, $\vec{Q}$ and ω are the twodimensional wavevector and energy of the elemen tary excitations characteristic of the substrate surface response and $U_Q(-z)$ is the coupling matrix element of the interaction potential which depends on a particular form of $q(\vec{r})$. $\vec{P}$ and $\vec{r}$ satisfy the usual commutation relations, while the operators $a_{\vec{Q}\omega}$ and $a^+_{\vec{Q}\omega}$ obey

$$[a_{\vec{Q}\omega}, a^+_{\vec{Q}'\omega'}]_- = \delta_{\vec{Q}\vec{Q}'}\delta(\omega-\omega') N_Q^{-1}(\omega) \qquad (3)$$

and describe the spectrum $S_Q(\omega)=\omega N_Q(\omega)/2$ of the substrate response which comprises a continuum of electron-hole pair excitations (e-h) and a coherent mode - surface plasmon of energy $\omega_Q /2/$. As is shown in Fig. 1, for a free electron surface the e-h part of the spectrum starts linearly with increasing ω,dominates up to $\omega \sim Qv_F$ (v_F=Fermi velocity), whereas for $\omega > Qv_F$ the surface plasmon contribution, which is sharply peaked around ω_s, is the dominant high-energy mode (ω_s=3-15 eV for normal metallic densities).

In order to find the reactive and dissipative components of the potential contained in H which govern the particle motion near the surface, we shall find it convenient to treat separately the virtual high energy excitations (mainly plasmons) from the real dissipative processes because the former, due to the low adparticle initial kinetic energy of the order kT, give rise only to the elastic potential scattering. Such a division is achieved by a canonical transformation /3/:

$$H' = e^{iS} H e^{-iS} \qquad (4a)$$

with

$$S = i \sum_{\vec{Q}} e^{i\vec{Q}\vec{\rho}} \int_{Qv_F}^\infty d\omega N_Q(\omega) \sqrt{U_Q(-z)/2\omega} \left(a_{\vec{Q}\omega} - a^+_{-\vec{Q}\omega}\right) , \qquad (4b)$$

which yields the Hamiltonian in the new representation:

$$H' = \frac{1}{2M}(\vec{P}-\vec{A})^2 + \phi(z) + \sum_{Q} \int_0^\infty d\omega \omega N_Q(\omega) \left(a^+_{\vec{Q}\omega} a_{\vec{Q}\omega} + \frac{1}{2}\right) +$$

$$+ \sum_{\vec{Q}} e^{i\vec{Q}\vec{\rho}} \int_0^{Qv_F} d\omega N_Q(\omega) \sqrt{\omega U_Q(-z)/2} \left(a_{\vec{Q}\omega} + a^+_{-\vec{Q}\omega}\right) . \qquad (5)$$

Here $\vec{A}(\vec{r})=-i\vec{\nabla}S(\vec{r})$ is a complex longitudinal vector potential with the properties $\vec{\nabla}\times\vec{A}=0$ and $\vec{\nabla}\cdot\vec{A}=0$ (Coulomb gauge) and:

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$$\phi(z) = -\sum_{\vec{Q}} U_Q(-z) \int_{Qv_F}^{\infty} d\omega \frac{S_Q(\omega)}{\omega} \qquad (6)$$

is a generalized image potential acting on the adparticle. The kinetic energy term can be written in the form

$$H'_{kin} = \frac{\vec{P}^2}{2M} - \vec{A}(\vec{r})\cdot\vec{v} + \frac{\vec{A}^2(\vec{r})}{2M}; \quad (\vec{v} = \frac{\vec{P}}{M}) \qquad (7)$$

since $\vec{P}$ and $\vec{A}$ commute. The second expression on the right-hand side of (7) is a friction term proportional to the velocity of the particle, often encountered in the studies of the motion of particles near dielectric surfaces. However, as in the present problem $kT \ll \omega_s$, this term will produce a negligible contribution to the energy dissipation compared with the last term on the right-hand side of (5) which describes the coupling of the particle motion to the continuum of the pair excitations of the substrate. On the other hand, the diagonal elements of the operator quadratic in $\vec{A}$ will contribute, together with $\phi(z)$, to the total reactive (adiabatic) potential V(z) acting on the adparticle centre of mass. Taking this into account, we obtain:

$$V(z) = \phi(z) + \frac{1}{2M}\sum_{\vec{Q}} |\vec{V}e^{i\vec{Q}\vec{\rho}}\sqrt{U_Q(-z)}|^2 \int_{Qv_F}^{\infty} d\omega \frac{S_Q(\omega)}{\omega^2} . \qquad (8)$$

Knowing $U_Q(-z)$ and $S_Q(\omega)$, one can calculate the adiabatic and dissipative potentials for the motion of a particle in the polarization field of the substrate electronic response.

3. Results and Discussion

As an example of our model, we carry out calculations for a simple adsorption system consisting of a free electron surface and a "rigid hydrogen" atom (with a single 1s level-orbital). These two assumptions enable us to estimate the matrix elements U_Q /4/ and use the formerly calculated surface response function /2/ in the calculation of the potential V(z) which is sketched in Fig. 2.

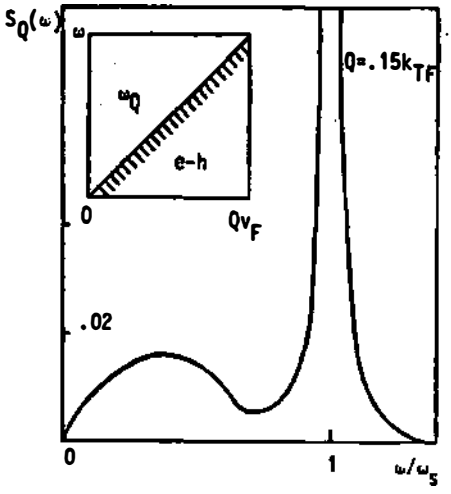

Fig.1: Spectrum of the surface response for a semi-infinite electron gas calculated in RPA.

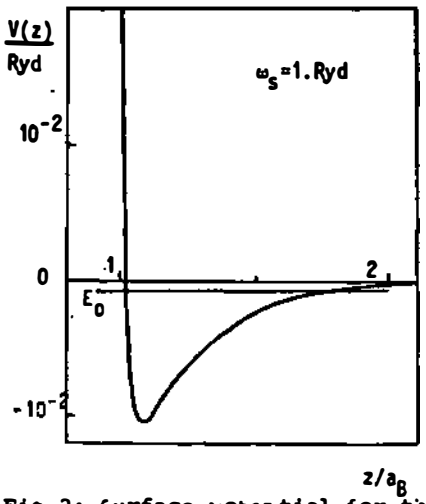

Fig.2: Surface potential for the adparticle derived from (8) for a substrate characterized by ω_s=1 Ryd.

The attractive part of the potential is due to the image screening of the atomic charge density (6), and the repulsive part arises as a consequence of the local enhancement of the atomic effective mass due to the particle dressing into a cloud of virtual, simultaneously emitted and reabsorbed surface plasmons. Solving numerically the Schrödinger equation for the particle at normal incidence to the surface, we find that V(z) is sufficiently attractive around its minimum to bind the atom in a localized state of energy E_o = = 0.000856 Ryd below the vacuum level.

The dissipative interaction described by the last term on the right-hand side of (5) will cause the decay of the particle from the initial state into the continuum states of lower energies or into the bound states. We have computed the transition probability Γ out of the initial state /5/ of energy $E \sim kT$ using model wavefunctions for the evaluation of the matrix elements appearing in the adparticle selfenergy $\Sigma(\omega)$. In Fig. 3 we have plotted $\Gamma(\omega)/2 = -\mathrm{Im}\Sigma(\omega)$. We have also found that the dominant component in Γ is $\Gamma_{i\to o}$ which describes the adparticle decay into the bound state. This is illustrated in Fig. 4 where we have sketched the ratio $\Gamma_{i\to o}/\Gamma$. The latter approaches unity in the interval of energies in which the adparticle decay rate from the initial state reaches its maximum. An important consequence of this feature, which follows directly from the unitarity of the evolution operator, is that the sticking probability s(t) approaches unity for times t exceeding the adparticle lifetime Γ^{-1}:

$$\lim_{t>\Gamma^{-1}} s(t) = 1 \ . \qquad (9)$$

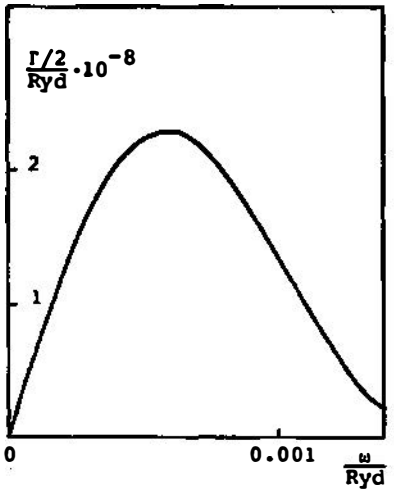

Fig.3: Imaginary part of the adparticle selfenergy for normal incidence.

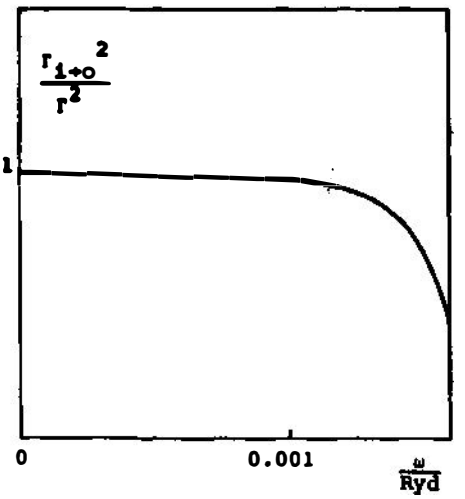

Fig.4: Square of the ratio of the sticking and total decay rates.

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