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Quantum size effect in the electron exchange between a H^- ion and a thin metal disk

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The resonant charge transfer (RCT) between a hydrogen anion and a thin aluminum disk is investigated by means of the wave-packet propagation method that does not exploit the perturbation theory. The RCT on a thin metal disk is found to exhibit quantum size effects due to the finite size of the disk. Survival amplitude of ion state has been calculated as a function of the distance to the ion-surface in a normal collision. It is shown that depending on the projectile velocity, the ion can interact with disk as if with bulk metal, thin film or nano-structure with the energy quantized by polar and normal coordinates.

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I. INTRODUCTION

RCT is one of the most important processes occurring during atom-surface interaction. The RCT process determines the charge state of scattered and sputtered particles that contains knowledge about elemental composition and structure, as well as about electronic properties of the surface. Besides the RCT process has a great impact on a number of phenomena occurring on a surface, that take place during secondary ion-emission, scattering, desorption, catalysis and surface modification.

At present the charge exchange between an atomic particle and bulk metal has been well studied.[1,2] Tunneling along the surface normal is energetically favorable, and an atomic electron propagates indefinitely deep into the metal. In this case, there is no possibility for a reverse electron transition to the atom. Electron transfer is qualitatively different for systems with finite size.[3,4] The blocking of electron propagation along the surface normal, which is the preferential direction for tunneling, should have the biggest effect on the RCT. One can mention the recent studies of the effect of the projected band gap along the surface normal for the (111) surfaces of noble metals. In that case, free electron propagation along the surface normal is not possible in a certain energy range and this leads to the existence of quantized states for perpendicular motion—surface and image states.[5] The latter generate two-dimensional (2D) electronic continua at the surface: electron motion confined to the directions perpendicular to the surface and quasifree parallel to the surface. The existence of a band gap and of 2D surface continua has been shown to lead to significant alterations in the RCT. The theoretically predicted quasiblocking of the RCT in certain systems and the dominance of the 2D surface state continuum in the RCT process[6–8] have been observed experimentally, both in scattering conditions.[9,10]

Island-films on a surface are an interesting example of systems with confined electron motion. A thin metal disk can be chosen as a physical model of such systems. This study is focused on determining certain features of the electron transfer between a negative hydrogen ion and an aluminum disk by means of the wave-packet propagation (WPP) method.[11,12] Specifically, some interesting relationships that demonstrate the quantum size effect can be obtained by varying the disk radius at a fixed disk thickness and a fixed distance between the atom and the disk. In the dynamic case (i.e. for a particle impinging on a surface) the influence of the projectile velocity on electron exchange is studied and the conditions required for the quantum size effect to be manifested are identified.

Section II below describes the problem and the method of solution. Section III is devoted to the results on the H^- ion-disk charge transfer for a fixed ion-surface distance (static situation), and Sec. IV addresses the results obtained for an ion moving in front of the surface (dynamic situation). Finally, Sec. V contains the concluding remarks.

II. THE PROBLEM FORMULATION AND SOLUTION

The goal is to calculate the electron transfer between a negative hydrogen ion and a metal disk. Electron energy inside the disk is quantized by two coordinates - normal and polar (z,ρ). It is necessary to know the quantized energy values for the problem analysis. As a first approximation one can assume that energy quantization by one coordinate doesn't depend on other coordinate. Therefore the set of discrete energy levels for normal coordinate coincides with discrete energy levels for a film of the same thickness.

In the *static situation* (fixed ion-surface distance) it is required to find the principal parameters of electron transfer such as the energy position (E) and ion-level width (Γ). Ion-level width characterizes the probability of electron transfer per unit of time ($\Gamma \sim 1/\tau$, where τ is the lifetime of an atomic electron). The differences resulting from the disk radius being finite can be revealed by comparing electron exchange on a thin disk with electron exchange on a thin film of the same thickness.[13,14] The presence of the quantum size effect can be determined by investigating how the principal electron exchange parameters depend on the disk radius.[15]

In the *dynamic situation* (ion is moving toward the surface) the goal is to understand how the projectile velocity influences the electron transfer. We assume that the hydrogen core approaches the surface from infinity along the surface normal to the disk center following a classical straight-line trajectory, at a constant velocity.[16] The charge state of hydrogen was calculated by WPP method (see description below). The previous studies have shown that projectile velocity essentially influences on charge exchange.[13] Moreover if the projectile velocity is high enough, electron transfer with lowdimension systems can be described by classical rate equation. The WPP analysis of ion-surface charge exchange for various collision velocities and its comparison with results obtained with rate equation for disk, film and bulk metal can be used to determine the projectile velocity impact on electron transfer and on whether the quantum size effect appears.

A. Rate equation

For a number of systems under study (e.g. bulk metal) the approach of wide-band can be used.[17,18] It can be shown that RCT process can be described by rate equation, with electron transfer rates depending on the level width of bound states:[19–21]

$$dP(t) = -\Gamma \cdot P(t) \cdot dt, \tag{1}$$

where $P(t)$ - is the probability of the state with electron remaining at the atomic particle, and Γ - is ion level width.

B. Wave-packet propagation (WPP) method

The WPP method consists in studying the time evolution of the electron wave function.[7,12] The time-dependent wave function $\psi_a(r,t)$ is a solution of the Schrödinger equation with the Hamiltonian

$$H = T + V_{e-H} + V_{e-surf}, \tag{2}$$

where $T = -\frac{1}{2}\Delta$ is the electron kinetic energy. $V_{e-H}(r) = -(1+1/r)\cdot\exp(-2r) - (\alpha_H/r^4)\cdot\exp(-r_0^2/r^2)$ is the interaction potential between an electron and an atomic core (r is the radial electron-atom distance in atomic units, $\alpha_H = 2.25$ and $r_0^2 = 2.547$).[11,22] The interaction potential between an electron and a disk V_{e-surf} is calculated as conjunction of conduction band bottom ($V_0 = 15.9$ eV) with classical self-image potential of the electron $(-1/4z)$ according to the Jennings approach.[23] Originally, Jennings potential is one-dimensional, so a superposition of Jennings potential along normal and polar coordinate is used in order to obtain two-dimensional disk potential. When the disk radius is extremely large the disk potential becomes identical to the potential of a film of the same thickness. This fact confirms the appropriateness of the above approach.

We consider a cylindrically symmetric case when the projection of electron angular momentum onto the symmetry axis is zero. The calculations are performed using the cylindrical coordinates $(\rho - z)$. The following substitution is used to improve the solution convergence

$$f(r,t) = \sqrt{\rho}\cdot\psi(r,t). \tag{3}$$

The Schrödinger equation is transformed accordingly:

$$i\frac{df(r,t)}{dt} = \widetilde{H}f(r,t), \tag{4}$$

$$\widetilde{H} = T_z + T_\rho + V_{e-H} + V_{e-surf}, \tag{5}$$

where

$$T_z = -\frac{1}{2}\frac{d^2}{dz^2}; \quad T_\rho = -\frac{1}{2\sqrt{\rho}}\frac{d}{d\rho}\left(\rho\frac{d}{d\rho}\right)\frac{1}{\sqrt{\rho}}. \tag{6}$$

The time behavior of the electron wave function is calculated using the evolutionary operator $U(\Delta t)$:

$$f(r,t+\Delta t) = U(\Delta t)\cdot f(r,t); \quad U(\Delta t) = \exp(-i\widetilde{H}\Delta t). \tag{7}$$

where Δt is the time step in numerical calculations.

To improve the accuracy of calculations, the evolutionary operator is divided into three components as

$$U(\Delta t) = \exp\left(-i\widetilde{H}_1\frac{\Delta t}{2}\right)\cdot\exp\left(-i\widetilde{H}_2\Delta t\right)\cdot\exp\left(-i\widetilde{H}_1\frac{\Delta t}{2}\right) + O(\Delta t^3), \tag{8}$$

where

$$\widetilde{H}_1 = T_z + V_{e-H} + V_{e-surf}; \quad \widetilde{H}_2 = T_\rho. \tag{9}$$

The exponential operators are estimated using the following procedure:

$$\exp(-i\widetilde{H}\Delta t) = \frac{1 - i(\Delta t/2)\widetilde{H}}{1 + i(\Delta t/2)\widetilde{H}} + O(\Delta t^3). \tag{10}$$

For numerically solving the Schrödinger equation, the wave function is calculated at discrete points of the $\rho - z$ space.

C. Eigenenergies and ion level width

In the static situation electron transfer is studied with a given initial electron wave function $\psi_a(r)$, which is the H^- outer electron wave function. The WPP method is used to determine $\psi(r,t)$. Then we determine the survival amplitude of the free-ion bound state or, equivalently, the electronic wave packet autocorrelation function

$$A(t) = \langle\psi_a(r)|\psi(r,t)\rangle, \tag{11}$$

and its Laplace transformation

$$g(\omega) = \frac{1}{\pi}\int_0^\infty dt e^{i\omega t}A(t) = \frac{1}{\pi}\int_0^\infty dt e^{i\omega t}\langle\psi_a(r)|\psi(r,t)\rangle, \tag{12}$$

The real part of $g(\omega)$ gives $n(\omega)$, that is the projected density of states (DOS). Note that the density $n(\omega)$ has a Lorentzian peak at the resonance position, i.e., at the energy of the quasibound state of hydrogen. It can be used to extract the resonance characteristics, that are (E) and (Γ). However, this procedure is accurate only if the propagation is calculated in a long time interval until the wave packet entirely leaves the atom in order to reach the convergence of Laplace transformation (12). This requires extremely long propagation times in the case of very narrow resonances. To avoid long propagation times, we analyze the autocorrelation function as the superposition of several exponential terms, with parameters determined using the least-squares method:

$$A(t) = \sum_{j=1}^{L} a_j \exp\{-i(E_j - i\Gamma_j)t\}. \tag{13}$$

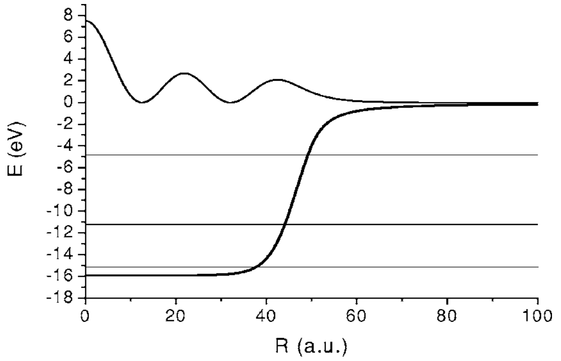

FIG. 1. Solution to the Schrodinger equation for a disk of 50 a.u. radius. The thick solid line shows the disk potential along the polar coordinate. Horizontal lines denote discrete energy levels below ion level (−1.3 eV). The solid curve shows a plot of the squared modulus of the wave function (arb. units) for upper energy level.

III. RESULTS FOR THE STATIC SITUATION

A considerable number of calculations have been made for a disk of 15 a.u. thickness (3 monolayers) and 50 a.u. radius; the ion-surface distance was 12 a.u. (Note that we use the atomic system of units with $m_e=e=\hbar=1$; 1 a.u. of distance equals to 0.53 Å, 1 a.u. of time equals to $2.419\cdot 10^{-17}$ s, and 1 a.u. of velocity equals to $2.188\cdot 10^{8}$ cm/s). The thickness value of 15 a.u. was chosen because the charge exchange with film of the same thickness was investigated in previous studies.[13,14] Hydrogen ion energy depends on the ion-surface distance as $E_a(z)=A-1/4z$, where A is the affinity level. Specifically, $E_a(12\text{ a.u.})=-1.3$ eV. The electron motion along the polar coordinate is quantized due to the finite disk radius, so discrete energy levels inside the disk arise. The energy restrictions should be taken into account: an electron can occupy only the discrete levels inside the disk with energy not higher than the ion level energy. There are three energy levels for the disk of 50 a.u. radius, which meet the energy restrictions (Fig. 1). The accuracy of the formulated energy restrictions is confirmed below (the electron occupies the highest available energy level inside the disk; this fact also confirms correctness of the chosen disk potential and the calculated energy levels).

Electron exchange between an atomic particle and a thin metal film was described in details in Ref. 13. Figure 2 shows the time evolution of electron transfer for an aluminum disk and an aluminum film of the same thickness. One can see that, during the initial stage of ion-surface interaction (up to 30 a.u. of time) no discrete features are observed on the surface. The wave function distributions for the disk and film are the same, and they correspond to the case of a bulk metal. To put it in a simpler way, the electron has no time to "sense" the finite size of the disk/film.

During the second stage (100 a.u. of time), the non-monotonic distribution of wave packet along the normal coordinate is visible for both disk and film, which results from discrete energy structure. However, the spatial distribution of the wave function for the disk remains identical to that for the film. The physical explanation for this is as follows: an electron reaches the remote disk/film border and, having reflected, continues its motion in the backward direction. Thus interference with a forward-moving wave packet occurs. From the beginning of the interference, the electron wave packet mainly propagates parallel to the surface. Until the radial boundary of the disk is reached, non-monotonic structures of electron density along the radial coordinate are not observed.

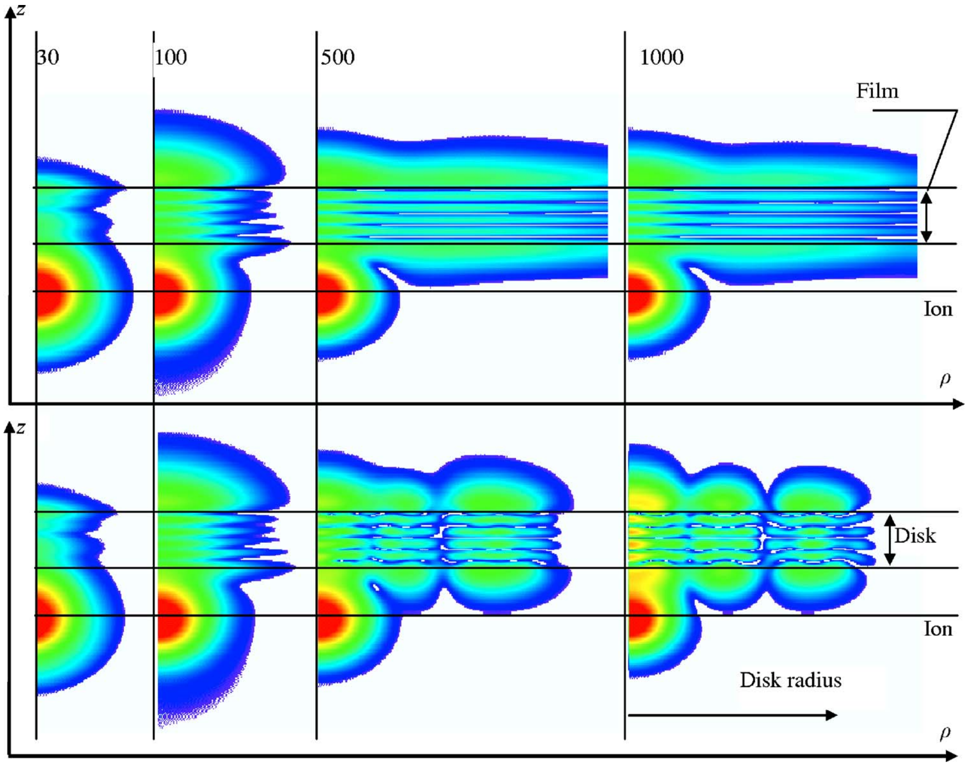

FIG. 2. (Color online) Capture dynamics for external electron of H^- for disk and film of 50 a.u. radius and 15 a.u. thickness. The patterns show the spatial distribution of an electron at subsequent moments of time (30, 100, 500 and 1000 a.u.). Darker regions correspond to regions where there is a higher probability of finding an electron. For clarity, the regions with a lower probability of finding an electron are shown in white. Solid lines show the ion geometrical position and disk/film boundaries. They are marked "film", "ion", "disk" (thickness), and "disk radius".

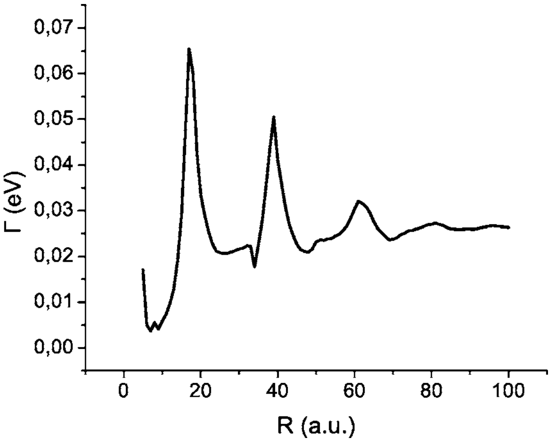

FIG. 3. Energy width Γ of H^- level as a function of disk radius. The disk thickness is 15 a.u.; the ion-disk spacing is 12 a.u.

The differences in charge transfer between the disk and the film become evident at the third stage of electron transfer, which lasts from 500 to 1000 a.u. of time. When the electron wave packet reaches the polar disk boundary, it is forced to move backwards to the center of the disk. Three electron-density maxima appear due to the interference along the polar coordinate. It should be stressed that the geometrical location and shape of these maxima corresponds to square modulus of the wave function of the highest energy level available in the disk (Fig. 1), so the electron mainly occupies the highest available energy level inside the disk. Note that the formation of a discrete structure over the polar coordinate always occurs after the discrete structure along the normal coordinate has been formed even in the case of the disk radius being smaller than the disk thickness. The reason for this is that the transfer of an electron along the surface normal is more energetically favorable. Thus, an electron, having been transferred to metal, continues to move until it reaches the remote boundary (stage 1). Then it moves in parallel to the surface (stage 2) and the discreteness along the polar coordinate becomes substantial (stage 3).

Quantum size effect

Ion-level width is shown in Fig. 3 as a function of disk radius. One can see that this function exhibits a non monotonic character (hydrogen level width as a function of thin film thickness also exhibits non monotonic character and abrupt variation[24]). A qualitative explanation for this dependence can be obtained considering the discrete structure of the energy levels inside the disk.

Resonant tunneling is known to be the primary channel of the charge transfer for the problem considered. An ion electron undergoes a transition from the ion level to the nearest available energy level inside the disk. Resonant-tunneling rate is determined by the difference between these two energy levels. This fact explains the non monotonic dependence of ion-level width on the disk radius. The maximal values of the level width coincide for those values of disk radius at which a new discrete energy level becomes available.[15] The difference between the ion energy level and the nearest energy level inside the disk is minimal at this moment. Thus electron transfer proceeds most efficiently due to resonance. The described dependence (Fig. 3) clearly demonstrates the quantum size effect during the electron exchange between an atomic particle and a thin metal disk, which is an example of a low-dimensional system.

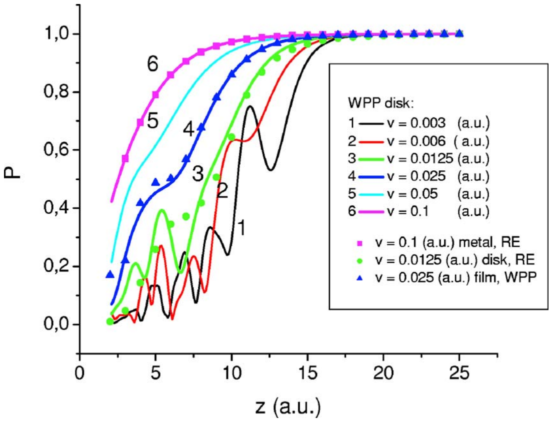

FIG. 4. (Color online) Survival probability for an H^- ion approaching a disk of 15 a.u. thickness and 50 a.u. radius. The solid curves are calculated using the WPP method. Squares and circles denote the solution of rate equation obtained using level width corresponding to static disk and bulk metal. Triangles correspond to WPP results for a film of 15 a.u. thickness (3 ML).

IV. DYNAMIC STUDY OF THE ELECTRON TRANSFER

WPP study was also applied to the case of an H^- ion approaching the surface at a constant perpendicular velocity. At the initial moment electron wave packet is distributed according to the H^- outer electron wave function. The calculations begin at the large ion-surface distance, where ion-surface interaction is negligible (as it was checked $z_{\mathrm{inf}} \geq 40$ a.u. certainly satisfy the above condition). The WPP provides the wave packet autocorrelation function $A(t)$ and survival amplitude $P(t)$

$$P(t) = |A(t)|^2. \tag{14}$$

Figure 4 presents the survival probability $P(t)$ of the H^- ion as a function of the distance as it approaches the surface for various collision velocities from 0.003 a.u. up to 0.1 a.u. (1 a.u. of velocity equals to $2.188 \cdot 10^8$ cm/s). One can see that projectile velocity substantially affects the electron exchange. If the collision velocity is high the exponential decay takes place, otherwise survival amplitude exhibits oscillations i.e., a transient recapture of the electron by the moving hydrogen occurs.

One can see that for the high projectile velocities (0.1 a.u.) electron transfer can be represented by rate equation with level width corresponding to bulk metal. Thus the projectile interacts so rapidly that there is no time to reveal the discrete structure of energy inside the disk and electron transfer occurs similarly for a thin disk, a film and bulk metal.

In the medium range of collision velocities (0.025 a.u.) the hydrogen survival amplitude dependence on ion-surface distance for a disk is close to the case of a film, but differs from the bulk metal case. Thus the ion-surface interaction is slow enough to feel the discrete structure of the film and disk along the normal coordinate. At the same time the interaction is sufficiently fast, to avoid the quantization along the polar coordinate, because the wave packet has not enough time to reach the disk radial boundary.

For the small collision velocities (less than 0.0125 a.u.) charge transfer between H^- ion and thin disk can be represented neither by rate equation nor by WPP calculation for a thin film.

Thus the dynamical system behavior qualitatively differs for various ranges of collision velocities: the specific disk characteristics that stipulate the quantum size effect have an effect at small collision velocities; while in the medium velocity range the disk acts as a film of the same thickness; and at high velocities charge exchange with a disk is similar to charge exchange with bulk metal.

V. CONCLUSIONS

This paper addresses the principal features of electron exchange between H^- ion and a thin metal disk. Both static (fixed ion-surface distance) and dynamic (ion is moving toward the surface) situations were investigated by means of wave-packet propagation method. The investigation performed leads us to the following conclusions about atomic-particle electron exchange with a thin metal disk:

(1) The electron transfer between a negative hydrogen ion and a thin disk is characterized by the formation of a discrete electron-density distribution, which has maxima along the coordinates (ρ, z). This is caused by interference of the wave packets.

(2) It has been shown that electron transfer between an ion and a thin disk starts to exhibit quantum size effect with disk radius changing. This quantum size effect exists only for small collision velocities.

(3) It is demonstrated that in the interaction between an ion and metal disk the charge transfer with the disk can proceed as charge transfer with bulk metal, thin film or nanostructure with energy quantized by two coordinates, depending on the projectile velocity.

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