Single Electron Capture by Back Scattered Protons from High-Melting Temperature Metals

KATO Daiji, SUNO Hiroya, KATO Takako, KIMURA Mineo[1] and TANABE Tetsuo[2†]

National Institute for Fusion Science, Toki 509-5292, Japan

[1] *Kyushu University, Fukuoka 812-8581, Japan*

[2] *Nagoya University, Nagoya 464-8603, Japan*

Abstract

Formation of excited hydrogen atoms above a tungsten surface was studied by means of the semi-classical theory. Occupation probabilities of the excited levels were calculated for proton velocities of 0.1 – 1.0 a.u.

Keywords:

1. Introduction

Excited state abundance in neutrals reflected at refractory metals has been an issue of study concerning the plasma-wall interaction in nuclear fusion devices. D_α emission has been observed from the reflected neutrals of a deuteron beam at a molybdenum surface [1]. However, the mechanism of the excited state formation has been little understood. Excited levels of the atomic hydrogen are above the Fermi level of the molybdenum by a few eV. Surface electrons hardly transfer to such the shallow levels via tunneling or classical-over-the-barrier, unless some surface impurities decrease the effective work function substantially. The effect of the surface impurities has not been studied in the present work; we have investigated other (non-trivial) mechanism first.

In the present work, the non-resonant single-electron transfer was studied by means of the semi-classical theory (electronic transition was treated quantum mechanically, while proton motion was represented by classical trajectories). Early studies on the electron transfer have been undertaken with the aid of simplified interaction matrix elements and/or the adiabatic approximation, *e.g.* Brako and Newns [2] and Burgdörfer *et al.* [3]. The present study is based upon direct numerical solutions of the time-dependent Schrödinger equation including accurate interaction potentials. We calculated occupation probabilities of the excited levels due to the non-resonant single-electron capture by a proton from a tungsten surface.

Atomic units ($\hbar = m_e = 1$) are used throughout unless otherwise stated.

2. Theoretical method

A hydrogen atom (a proton and an electron) above a metal surface is illustrated in Fig. 1. The electron moves under influences of three potentials: the Coulomb attractive potential of a proton, the attractive potential of the surface dipole layer and the exchange-correlation effect (V_e^I), and repulsive potential of a pile of electron density at the surface induced by the proton (V_p^I). The semi-empirical formula is used for V_e^I of tungsten proposed by Jennings *et al.* [4],

$$V_e^I(x) = \frac{1}{2} \begin{cases} \left(1 - e^{\lambda(x-x_0)}\right)/2(x-x_0), & x < x_0 \\ -2V_0\left(1 + Ae^{-B(x-x_0)}\right)^{-1}, & \text{otherwise,} \end{cases}$$

(1)
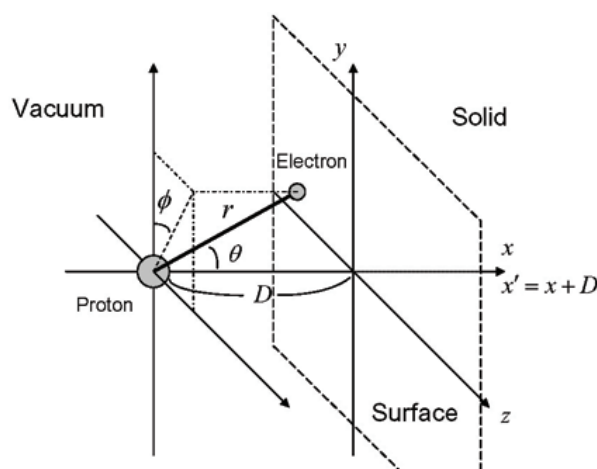
where $A = 4V_0/\lambda - 1$ and $B = 4V_0/A$ are constants de-

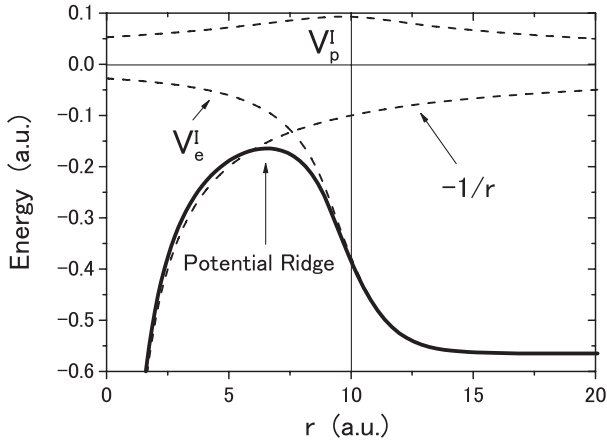Fig. 1 Coordinate system of a hydrogen atom above a metal surface.

Fig. 2 Effective potential of electron for tungsten surface along x-axis ($\theta = 0$ geometry). Bold solid line is sum of the three potentials. $D = 10$ a.u.

termined by matching the potential and its derivative at $x = x_0$. $x_0 \approx -0.93$ is the position of the image plane and $|x_0|$ was determined using an empirical formula by Ossicini *et al.* [5]. $V_0 \approx 0.565$ a.u. is given by the sum of the Fermi energy and the work function of tungsten. $\lambda \approx 1$ is obtained by fitting Eq. (1) to an planar averaged potential of the linearized augmented-plane-wave calculation [4]. V_p^I is obtained from the static linear density response function of the conduction electrons whose Kohn-Sham wave functions are calculated using the V_e^I [6]. The potentials are shown in Fig. 2 for tungsten.

Electronic wave functions are written in the spherical coordinates whose origin is located at the proton. Geometry of the electronic system is restricted to $\theta = 0$; the angular freedom of motion is omitted in the present model. Because of the lowest effective potential barrier, the electron transfer takes place most probably along x-axis ($\theta = 0$ geometry). Accordingly, the one-dimensional Schrödinger equation for each proton-surface distance D is written as,

$$\left\{ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} + V_e^I(r; D) + V_p^I(r; D) \right\} \Phi(r; D)$$

$$= \epsilon(D) \, \Phi(r; D). \tag{2}$$

A set of discrete eigen-energies ϵ are obtained by solving Eq. (2) in a finite radial coordinate range, $r \in [0, R]$, under boundary conditions of $\Phi(0; D) = 0$ and $\Phi^{-1} d\Phi/dr|_{r=R} = a$, where a is a constant. To represent dissipation of the atomic state near the surface, the outgoing wave boundary condition is imposed to the wave function, $(d/dr - ik) \Phi|_{r=R} = 0$, where $k = \sqrt{2\epsilon}$ measured from $-V_0$. As a result, the Hamiltonian matrix of Eq. (2) becomes quadratic of k. It is transformed to the linear non-Hermitian matrix equation of k [7], and

solved numerically using the discrete-variable representation [8] of the Jacobi-polynomial. Figure 3 shows the calculated eigen-energies (real part of k^2) and broadening of the atomic levels (imaginary part of $-k^2$) as a function of D for the tungsten surface. The eigen-energies separate into energy levels of the atomic hydrogen and discretized energy levels of the conduction electrons at large D values. On the other hand, near the surface, the atomic levels are broadened as well as shifted by the surface potentials.

The motion of the proton is represented by classical trajectories, as the de Broglie wavelength is much shorter than the atomic scale for proton energies considered here (>100 eV). Once excited hydrogen atoms dive into the metal, electrons at the excited levels are stripped immediately due to the strong screening effect of conduction electrons. Thus, only outgoing part of
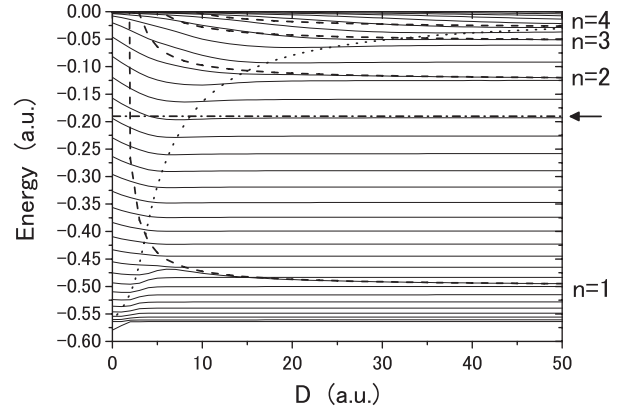

Fig. 3 (a) Eigen-energies for tungsten surface as a function of D. Solid curves are the eigen-energies, dashed curves atomic hydrogen levels shifted by the classical image potential, a dotted curve the top of the potential ridge (see Fig. 2), and a dashed-dotted line the Fermi level of tungsten (about −0.19 a.u.).
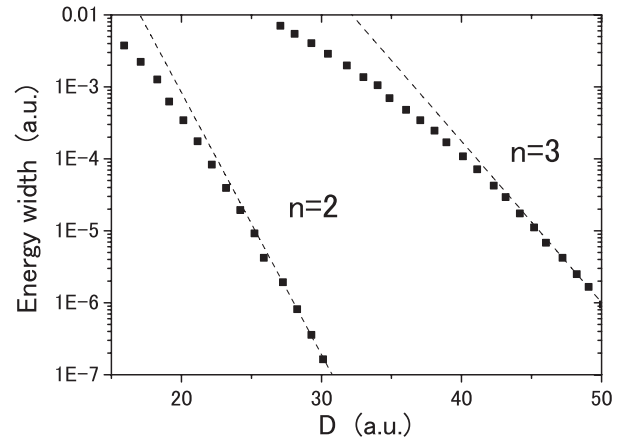

Fig. 3 (b) Level broadening of atomic hydrogen above tungsten surface as a function of D. Dotted lines are fitting to exponential functions of D.

the trajectory is relevant to the excited hydrogen atoms emitted from the surface. For simplicity, we use the straight line trajectory normal to the surface. The velocity change of the proton due to the image force and electronic transition is omitted, since it may be not significant for the proton energies considered here.

At the starting time t_0, the proton is placed just above the surface with a small distance of D_0, and then recedes from the surface with a constant velocity of $v < 0$. The initial electronic state of the hydrogen-tungsten system is assumed to be in the ground state: All electronic levels below the Fermi level of the tungsten are equally occupied, while higher levels are empty. The initial wave function is expanded in terms of the eigen-state wave function at D_0,

$$\Psi(x, t_0) = e^{-ivx+iv^2/2t_0} \sum_k \Phi_k(r; D_0) e^{i\sigma_k} \Theta(\epsilon_F - \epsilon_k(D_0)),$$
(3)

where $e^{-ivx+iv^2/2t_0}$ is a kinematical factor to meet the Galilean invariance of the time-dependent Schrödinger equation. In the present study, we included about 300 eigen-states in the expansion. The random phase approximation is applied to the initial state. The wave function is propagated numerically in the time domain using the split-operator spectral method [9]. At a sufficiently large D (after a long time t), the occupation probabilities of the atomic levels are obtained by projecting $\Psi(t)$ on to $\Phi_k(D(t))$, and those of the conduction levels by projecting on to $e^{-ivx+iv^2/2t}\Phi_k(D(t))$.

3. Results and discussion

Present calculations were performed for a tungsten slab whose width is about 100 a.u. (about 5 nm). Figure 4 shows the occupation probabilities of the atomic levels as a function of the proton velocity. At low velocities, the occupation probability of the ground level is almost unity, whereas those of the excited levels are
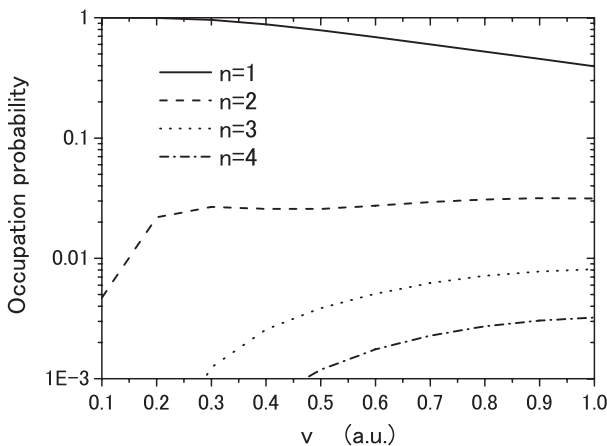
vanishingly small as expected in the adiabatic approximation. As the velocity increases, the probabilities of the excited levels grow, while that of the ground level declines. The enhancement of the non-resonant electron transfer to the higher excited levels may be explained as follows. Near the surface, top of the potential ridge lying between the proton and the surface dives below the Fermi level (see Fig. 3(a)). As the proton recedes from the surface, the top rises out of the Fermi level. Faster the proton recedes from the surface, more the electronic wave function is kept sitting astride of the potential ridge and elevated to the higher atomic level. The wave function astride of the potential ridge represents a diabatic state which is promoted to the higher excited levels along the top of the potential ridge.

A hump is seen in the $n = 2$ occupation probability at low velocities. It may be attributed to the oscillatory transition between quasi-resonant states of the $n = 2$ level and a discrete conduction level of the metal slab. With the larger slab width (the higher number density of the conduction levels), the hump becomes less significant. For the semi-infinite metal, the hump should disappear after the transition amplitude is integrated over the continuous conduction band in which the atomic levels are embedded (bandwidth effect).

As a concluding remark, it is noted that the present model is based upon the dispersion relation of the quasi-free electron-gas. However, transition metals like tungsten have substantially different density of states from that of the free electron-gas. An improved model taking account of a correct density of states is under development. The Auger deexcitation might depopulate the excited levels, while it is left for future studies. To compare the present occupation probability of the $n = 3$ level (Fig. 4) with the D_α emission measurement, i.e. Ref. [1], the velocity distribution of reflected hydrogen atoms must be taken into account. The comparison will be made in future studies.

Fig. 4 Level occupation of atomic hydrogen emitted from tungsten surface.

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