

Time-dependent density functional theory simulation for analyzing the neutralization process of hydrogen ions injected onto tungsten surfaces

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We conducted time-dependent density functional theory simulations to investigate the neutralization process of a hydrogen ion injected at 100 eV onto the (110) surface of tungsten. Additionally, we introduced a method for evaluating the detection probability of electrons within a localized region. This probability serves as an indicator for identifying hydrogen in its various states: positive ion, neutral atom, and negative ion. Our findings indicate that following the collision, the probabilities of detecting hydrogen as a positive ion, neutral atom, and negative ion are approximately 25%, 50%, and 25%, respectively.

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I. INTRODUCTION

Atomic-scale plasma-material interaction (PMI) simulations have traditionally employed the binary collision approximation (BCA) for modeling physical sputtering, molecular dynamics (MD) for incorporating many-body effects such as chemical sputtering, and density functional theory (DFT) for achieving higher accuracy in calculations [1–3]. In previous PMI simulations, neutral atoms have often been used as substitutes for injected ions from plasma, based on the assumption that ions undergo rapid neutralization upon contact with material surfaces. However, experimental studies have demonstrated that incident ions may be reflected not only as neutral atoms, but also as ions that either retain their charge or undergo reionization after neutralization [4]. Although several theoretical models have attempted to describe the neutralization process of incident ions on a surface [5–8], the mechanism remains insufficiently understood.

To accurately model PMI processes that account for ion neutralization, capturing the real-time dynamics of electrons at the material surface is essential. One theoretical framework capable of addressing such dynamic electron behavior is time-dependent density functional theory (TDDFT) [9]. Here, TDDFT can be broadly classified into two approaches: linear-response TDDFT (LR-TDDFT) and real-time TDDFT (RT-TDDFT). LR-TDDFT is a method that calculates the first-order response to a time-dependent external potential. In this study, since the positions of the nuclei also change over time, we adopted RT-TDDFT, in which the time-dependent Kohn-Sham equations are directly integrated numerically to

compute the time evolution of the electronic orbitals. In addition, RT-TDDFT is, in principle, capable of describing higher-order responses compared to LR-TDDFT, and is therefore suitable for complex processes such as neutralization. Hereafter, TDDFT refers to RT-TDDFT unless otherwise noted.

Pioneering research on TDDFT-based ion injection simulations in PMI was reported by Miyamoto *et al.* [10,11], who investigated the incidence of Ar^{7+} on graphene at 5 and 500 keV. Their simulations confirmed the excitation of the argon ion upon collision with the graphene surface. Another TDDFT-based study explored the incidence of hydrogen atoms on graphene at 30 eV–3 keV [12], comparing DFT simulations using the Born-Oppenheimer approximation (BO-DFT) and TDDFT. The results indicated that energy transfer from the incident particle to the target was more pronounced in TDDFT than in BO-DFT simulations. This approach enables the execution of PWI simulations to analyze the ion neutralization process at solid surfaces.

We are particularly rooted in fusion research within the field of PMI, and in fusion, we are interested in hydrogen and its isotopes as fuel species. To bring fusion reaction, deuterium and tritium are used, but in laboratory experimental devices, protium is often used. We also have a strong interest in helium plasma, which is a fusion reaction product. PMI in fusion refers to the interaction between such hydrogen and helium plasmas and the inner wall of the vacuum vessel that confines them. Currently, tungsten is the main material used for the inner wall. This is particularly referred to as plasma-wall interaction (PWI), which has been studied extensively, and the interaction between tungsten and hydrogen isotopes is of great interest.

In fusion reactors, the inner wall is generally classified into the divertor plates and the first wall. For example, in the case of ITER, under typical discharge conditions, ions incident on the divertor are expected to be accelerated by the sheath to energies exceeding 15 eV. On the other hand, in the first wall, there is variation, and the typical incident energy is

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estimated to be 8–300 eV [13]. Therefore, many experiments and simulations have been conducted in the energy range from several eV to several keV in the context of PWI [1,14]. This energy range is also common in semiconductor processes.

Based on this background, in this study we selected tungsten as the target material and used the most stable surface orientation, W(110), as the surface. The incident particle was chosen to be a hydrogen ion, and the incident energy was set to 100 eV, which lies in the middle of the typical energy range.

In this study, we investigate hydrogen ion impact, whereas the previous work [15] focused on helium ion impact. In the field of PWI, the difference between H and He is considered highly significant and goes beyond a simple difference in charge. For example, although helium can readily capture two electrons, hydrogen capturing two electrons is classically unstable. However, the hydrogen negative ion (H^-) does exist and is stabilized by quantum mechanical effects. While the mechanism of H^- formation has been studied from various perspectives, a decisive understanding has not yet been reached in our field, and it remains an important issue. Moreover, from an experimental standpoint, it is a key factor in negative ion beam sources [16]. In this work, we aim not only to study the neutralization process, but also to contribute to the understanding of H^- formation. Section II outlines the framework of PWI simulations based on TDDFT. Section III presents the theoretical foundation for calculating electron detection probability in an N -electron quantum many-body system, which serves as the basis for determining the state of each atom through the probability of electron existence around its nucleus. In Sec. IV, we present and discuss the simulation results for the neutralization process of hydrogen ions on a tungsten surface using TDDFT, focusing on the estimated neutralization probability of the incident hydrogen ion. Finally, Sec. V summarizes the main findings and discusses potential directions for future research.

II. SIMULATION METHOD

Simulating the neutralization process of ions injected from plasma onto material surface requires simultaneously solving both electron wave-function dynamics and nuclei classical motion.

Therefore, we adopt a simulation approach of the Ehrenfest MD, in which the time evolution of electron wave functions is solved by TDDFT and the equation of motions of nuclei are solved by MD [17], as follows:

The evolution of electron wave functions is governed by the time-dependent Kohn-Sham (TDKS) equation

$$i \frac{\partial \psi_j(x, t)}{\partial t} = \hat{H}_{KS} \psi_j(x, t), \quad (1)$$

where $\psi_j(x, t)$ ($j = 1, 2, \dots, n$) represents the j th TDKS orbital, and x_i represents the spatial coordinate r_i and the spin variable σ_i ($i = 1, 2, \dots, n$). $\hat{H}_{KS}$ denotes the KS Hamiltonian

$$\hat{H}_{KS} = -\frac{1}{2} \Delta + \hat{V}_H[\rho] + \hat{V}_{xc}[\rho] + \hat{V}_l + \hat{V}_{nl}. \quad (2)$$

Here $\hat{V}_H[\rho]$ is Hartree potential, $\hat{V}_{xc}[\rho]$ is exchange-correlation potential, and $\hat{V}_l$ and $\hat{V}_{nl}$ are local and nonlocal terms of pseudopotential, respectively. The motion of the

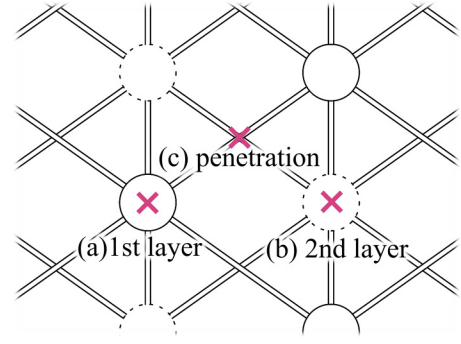


FIG. 1. Three kinds of incident conditions. Solid and dashed circles represent atoms of the first and second layer, respectively. (a) An incident from directly above the tungsten atom in the first layer, (b) an incident from directly above the tungsten atom in the second layer, and (c) an incident from the center of the two nearest atoms in the first layer. The incident angle is perpendicular to the (110) surface in all cases.

nuclei is described by Newton's equation

$$M_\alpha \frac{d^2 \vec{R}_\alpha}{dt^2} = -\frac{\partial}{\partial \vec{R}_\alpha} \{E_{nn}(\vec{R}) + E_{KS}[\rho]\}, \quad (3)$$

where $E_{nn}(\vec{R})$ represents the interaction energy among nuclei [15], $E_{KS}[\rho]$ is the KS energy functional of the electron density ρ , M_α is mass of α th nucleus, $\vec{R}_\alpha$ is coordinate of α th nucleus, and $\vec{R}$ is the collection of nuclear positions.

In this study, Ehrenfest MD calculations were performed using the QUMASUN code [15]. It employed the Leapfrog integration to calculate the time evolution of the motion of nuclei while simultaneously calculating the time evolution of the KS orbitals. Specifically, the TDKS orbitals and nuclei coordinates and momenta are updated by the following difference equation:

$$\vec{R}_\alpha \left(t + \frac{1}{2} \Delta t \right) = \vec{R}_\alpha(t) + \frac{1}{2} \Delta t \frac{\vec{P}_\alpha(t)}{M_\alpha}, \quad (4)$$

$$\psi_j(x, t + \Delta t) = \psi_j(x, t) + \sum_{k=1}^4 \frac{1}{k!} (-i\Delta t)^k H_{KS}^k \psi_j(x, t), \quad (5)$$

$$\vec{P}_\alpha(t + \Delta t) = \vec{P}_\alpha(t) - \frac{\partial}{\partial \vec{R}_\alpha} \{E_{nn}(\vec{R}) + E_{KS}[\rho](\vec{R})\} \Delta t, \quad (6)$$

$$\vec{R}_\alpha(t + \Delta t) = \vec{R}_\alpha \left(t + \frac{1}{2} \Delta t \right) + \frac{1}{2} \Delta t \frac{\vec{P}_\alpha(t + \Delta t)}{M_\alpha}. \quad (7)$$

Here, $\vec{P}_\alpha$ is the momentum of α th nucleus, E_{nn} is the potential energy of nuclei interaction, and E_{KS} is KS total energy of total electron.

The target material is the (110) surface of tungsten, comprising 48 atoms and 576 electrons. Tungsten crystallizes in a body-centered-cubic (bcc) structure, with a lattice constant of 5.97 bohrs. A hydrogen ion is injected perpendicularly onto the surface with an incident energy of 100 eV. Simulations are conducted for three distinct incident positions: (a) directly above a tungsten atom in the first layer, (b) directly above a tungsten atom in the second layer, and (c) within the gap between tungsten atoms (Fig. 1). In cases (a) and (b), the

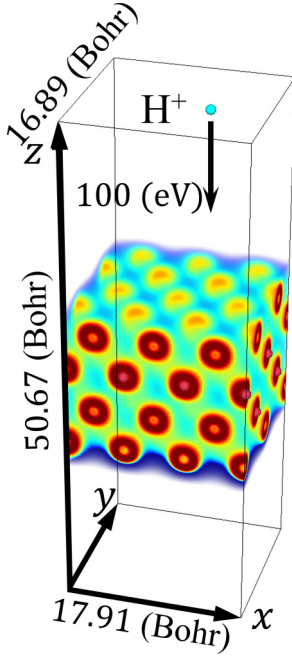


FIG. 2. Simulation system. The blue and red spheres indicate the hydrogen ion and tungsten atoms, respectively. The color map is a volumetric rendering of the electron density (integrated along the line of sight) for visualization of the 3D structure.

incident ion undergoes direct collision with a tungsten atom under conditions where the impact parameter is zero. In case (c), the incident ion penetrates the material via channeling. The time step for the simulation is 2.41×10^{-19} s. The dimensions of the simulation box are $17.891 \times 16.89 \times 50.67$ bohrs³ (see Fig. 2), with a spatial grid resolution of $60 \times 60 \times 180$. The exchange-correlation term is described by the local spin density approximation [18]. The frozen-core approximation is applied, employing the Morrison-Bylander-Kleinman pseudopotential [19], a norm-conserving pseudopotential generated using ADPACK for OPENMX [20,21]. In this study, we employed a tungsten pseudopotential generated with an explicit treatment of 12 valence electrons.

The initial state of the system is generated in two steps. First, the relaxed structure of the tungsten surface is obtained via DFT calculations, incorporating a vacuum region of 23.88 bohrs. Next, a hydrogen ion is positioned at the predefined incident locations (a), (b), or (c) within the simulation box. The z coordinate of the hydrogen ion is set to 50.0 bohrs in all cases, corresponding to a distance of 20.7 bohrs from the tungsten surface. The system initialization follows this procedure.

III. ANALYSIS METHOD FOR DETECTION PROBABILITIES OF ELECTRONS

This study aims to estimate the neutralization probability of an incident hydrogen ion after its collision with the tungsten surface by analyzing the electron wave function. Consider a small spatial region, denoted as V , that encloses a hydrogen nucleus, while the rest of the system is designated as $\bar{V}$ (see Fig. 3). If no electrons are detected within V , the hydrogen is interpreted as a positive ion. If one electron is detected

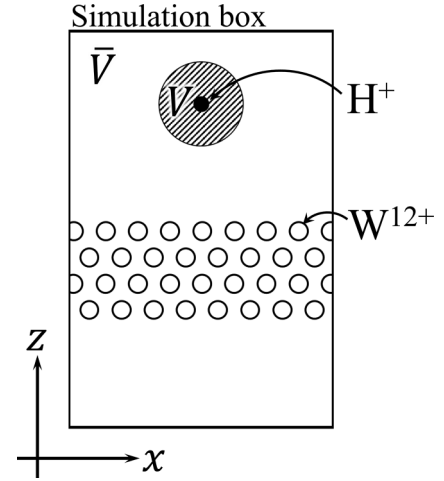


FIG. 3. The hatched region represents the small region V containing hydrogen, which is used in the evaluation of the detection probability. The rest of the region is $\bar{V}$.

within V , the hydrogen is interpreted as a neutral atom. If two electrons are detected within V , the hydrogen is interpreted as a negative ion. In a quantum many-body system, the probability of detecting m electrons in V is expressed as

$$P(m) = \binom{n}{m} \prod_{i=1}^m \int_V dr_i \prod_{j=m+1}^n \int_{\bar{V}} dr_j p(r_1, r_2, \dots, r_n). \quad (8)$$

For hydrogen, $P(0)$, $P(1)$, and $P(2)$ correspond to the probabilities of detecting a positive ion, neutral atom, and negative ion, respectively. The probability density function is given by

$$p(r_1, r_2, \dots, r_n) = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_n} \Psi^*(x_1, x_2, \dots, x_n) \times \Psi(x_1, x_2, \dots, x_n). \quad (9)$$

The all-electron wave function is approximated using a Slater determinant

$$\Psi(x_1, x_2, \dots, x_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(x_1) & \dots & \psi_1(x_n) \\ \vdots & \ddots & \vdots \\ \psi_n(x_1) & \dots & \psi_n(x_n) \end{vmatrix}, \quad (10)$$

where $\psi_i(x)$ represents the TDKS orbital. The TDKS orbital $\psi_i(x)$ is the product of a spin function $f_i(\sigma)$ and a spatial orbital $\phi_i(r)$. In this study, the TDKS orbitals are obtained using TDDFT. In our simulation, we assume that the first a TDKS orbitals correspond to up-spin states, while the remaining $n-a$ orbitals correspond to down-spin states:

$$f_i(\sigma) = \begin{cases} \alpha(\sigma) & \text{if } 1 \leq i \leq a, \\ \beta(\sigma) & \text{if } a+1 \leq i \leq n, \end{cases} \quad (11)$$

where $\alpha(\sigma)$ and $\beta(\sigma)$ denote the up-spin and down-spin functions, respectively.

Next, the integration for $\bar{V}$ can be divided into full-space and V components:

$$\prod_{j=m+1}^n \int_{\bar{V}} dr_j = \prod_{j=m+1}^n \left(\int dr_j - \int_V dr_j \right). \quad (12)$$

We introduce the function

$$\eta(s) = \sum_{1 \leq k_1 < k_2 < \dots < k_s \leq n} \sum_{\tau} \text{sgn}(\tau) \prod_{i=1}^s \langle \psi_{k_i} | \psi_{\tau(k_i)} \rangle_V, \quad (13)$$

$$\begin{aligned} \langle \psi_i | \psi_j \rangle_V &= \sum_{\sigma} \int_V dr \psi_i^*(x) \psi_j(x) \\ &= q_{ij} \sum_{\sigma} f_i(\sigma) f_j(\sigma), \end{aligned} \quad (14)$$

$$q_{ij} = \int_V \psi_i^*(r) \psi_j(r), \quad (15)$$

where τ is a permutation of $(k_1, k_2, \dots, k_s)$ to $(\tau(k_1), \tau(k_2), \dots, \tau(k_s))$ and the summation $\sum_{\tau}$ extends over all such permutations. Using Eq. (12) along with the binomial theorem, Eq. (8) can be reformulated as

$$P(m) = \sum_{s=m}^n \frac{(-1)^{s-m} s!}{m!(s-m)!} \eta(s) \quad (16)$$

$$\begin{aligned} &= \eta(m) + (m+1)\eta(m+1) + \frac{(m+2)(m+1)}{2} \\ &\quad \times \eta(m+2) + O(\langle \psi_i | \psi_j \rangle_V^{m+3}). \end{aligned} \quad (17)$$

Since $\eta(s)$ represents the s th-order term of $\langle \psi_i | \psi_j \rangle_V$, an approximation of up to order $m+2$ is employed in this study. The range of $\langle \psi_i | \psi_j \rangle_V$ is $0 \leq \langle \psi_i | \psi_j \rangle_V \leq 1$. If $\langle \psi_i | \psi_j \rangle_V$ is sufficiently small, the $m+2$ order approximation provides a reasonable estimation.

The aforementioned formulation for electron detection probability is derived from spin-polarized TDKS orbitals from TDDFT. However, when considering the detected electrons, we do not distinguish between up spin and down

spin. Instead, the primary focus is on the total number of detected electrons. For cases requiring spin-specific analysis, the probability $P(\mu, \nu)$ of detecting μ up-spin electrons and ν down-spin electrons within V can be derived as a component of $P(m)$. This formulation explicitly distinguishes between the spins of the detected electrons. First, the all-electron wave function (10) can be expanded using the Slater determinants $\Psi_{\uparrow}(x_{i_1}, x_{i_2}, \dots, x_{i_a})$ and $\Psi_{\downarrow}(x_{i_{a+1}}, x_{i_{a+2}}, \dots, x_{i_n})$, which consist solely of up- and down-spin orbitals, respectively. Specifically, it can be written as

$$\begin{aligned} &\Psi(x_1, x_2, \dots, x_a) \\ &= \frac{\sqrt{a!} \sqrt{b!}}{\sqrt{n!}} \sum_{1 \leq i_1 < i_2 < \dots < i_a \leq n} (-1)^{1+2+\dots+a+i_1+i_2+\dots+i_a} \\ &\quad \times \Psi_{\uparrow}(x_{i_1}, x_{i_2}, \dots, x_{i_a}) \Psi_{\downarrow}(x_{i_{a+1}}, x_{i_{a+2}}, \dots, x_{i_n}). \end{aligned} \quad (18)$$

Substituting this into Eq. (9), we get

$$\begin{aligned} p &= \sum_{1 \leq i_1 < i_2 < \dots < i_a \leq n} \frac{a!b!}{n!} p_{\uparrow}(r_{i_1}, r_{i_2}, \dots, r_{i_a}) \\ &\quad \times p_{\downarrow}(r_{i_{a+1}}, r_{i_{a+2}}, \dots, r_{i_n}), \end{aligned} \quad (19)$$

where

$$p_{\uparrow}(r_1, r_2, \dots, r_a) = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_a} |\Psi_{\uparrow}(x_1, x_2, \dots, x_a)|^2, \quad (20)$$

$$\begin{aligned} &p_{\downarrow}(r_{a+1}, r_{a+2}, \dots, r_n) \\ &= \sum_{\sigma_{a+1}} \sum_{\sigma_{a+2}} \dots \sum_{\sigma_n} |\Psi_{\downarrow}(x_{a+1}, x_{a+2}, \dots, x_n)|^2. \end{aligned} \quad (21)$$

Focusing on the sum in Eq. (19), we see that it represents the joint probability density for electrons $i_1, i_2, \dots, i_a$ to be spin up and electrons $i_{a+1}, i_{a+2}, \dots, i_n$ to be spin down, with their respective positions at $r_{i_1}, r_{i_2}, \dots, r_{i_a}$ and $r_{i_{a+1}}, r_{i_{a+2}}, \dots, r_{i_n}$. Using this fact, $P(\mu, \nu)$ can be written as

$$\begin{aligned} P(\mu, \nu) &= \sum_{1 \leq i_1 < i_2 < \dots < i_a \leq n} \frac{a!b!}{n!} \binom{a}{\mu} \binom{b}{\nu} \int_V dr_{i_1} \dots \int_V dr_{i_{\mu}} \int_{\bar{V}} dr_{i_{\mu+1}} \dots \int_{\bar{V}} dr_{i_a} p_{\uparrow}(r_{i_1}, r_{i_2}, \dots, r_{i_a}) \\ &\quad \times \int_V dr_{i_{a+1}} \dots \int_V dr_{i_{a+\nu}} \int_{\bar{V}} dr_{i_{a+\nu+1}} \dots \int_{\bar{V}} dr_{i_n} p_{\downarrow}(r_{i_{a+1}}, r_{i_{a+2}}, \dots, r_{i_n}). \end{aligned} \quad (22)$$

Hence, $P(\mu, \nu)$ can be expressed as the product of $P_{\uparrow}(\mu)$, which represents the probability of detecting μ up-spin electrons within V , and $P_{\downarrow}(\nu)$, which denotes the probability of detecting ν down-spin electrons:

$$P(\mu, \nu) = P_{\uparrow}(\mu) P_{\downarrow}(\nu), \quad (23)$$

where

$$P_{\uparrow}(\mu) = \sum_{s=\mu}^a \frac{(-1)^{s-\mu} s!}{\mu!(s-\mu)!} \eta_{\uparrow}(s), \quad (24)$$

$$P_{\downarrow}(\nu) = \sum_{s=\nu}^b \frac{(-1)^{s-\nu} s!}{\nu!(s-\nu)!} \eta_{\downarrow}(s), \quad (25)$$

$$\eta_{\uparrow}(s) = \sum_{1 \leq k_1 < k_2 < \dots < k_s \leq a} \sum_{\tau} \text{sgn}(\tau) \prod_{i=1}^s q_{k_i \tau(k_i)}, \quad (26)$$

$$\eta_{\downarrow}(s) = \sum_{a+1 \leq k_1 < k_2 < \dots < k_s \leq n} \sum_{\tau} \text{sgn}(\tau) \prod_{i=1}^s q_{k_i \tau(k_i)}. \quad (27)$$

Here, $\sum_{1 \leq k_1 < \dots < k_s \leq a}$ and $\sum_{a+1 \leq k_1 < \dots < k_s \leq n}$ represent a summation over all sets of s integers $(k_1, k_2, \dots, k_s)$ such that

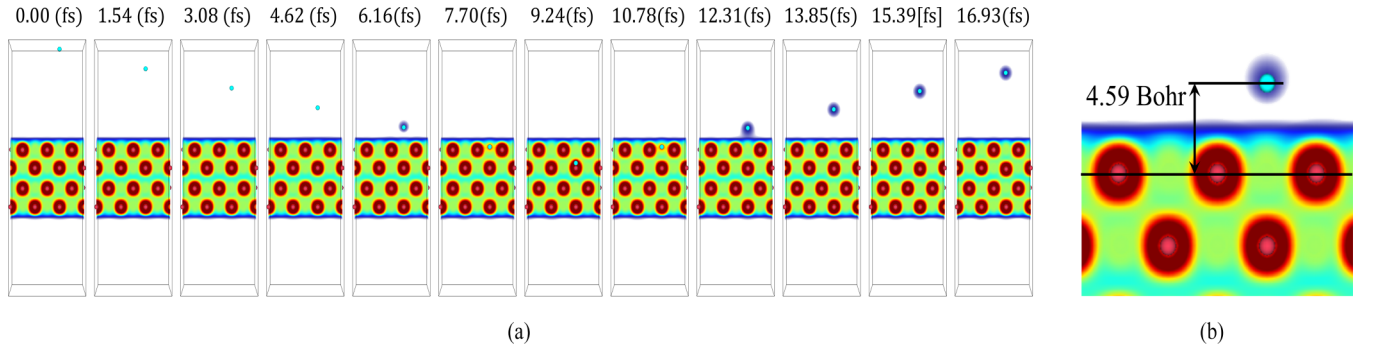


FIG. 4. Snapshots of the TDDFT and MD combined simulation for the incidence of a hydrogen ion onto a tungsten surface in case (b). The blue and red solid spheres indicate the hydrogen and tungsten nuclei, respectively. The colored area around the nucleus is the electronic density. The figure is the cross section of the simulation box parallel to the xz plane whose y coordinate is the same as that of the hydrogen nucleus. (a) Time evolution of electron density (b) Electron density around hydrogen at $t = 6.16$ fs.

$1 \leq k_1 < \dots < k_s \leq a$ and $a + 1 \leq k_1 < \dots < k_s \leq n$, respectively. Furthermore, there is a relationship between $P(m)$ and $P(\mu, \nu)$ given by

$$P(m) = \sum_{\mu=0}^m P_{\uparrow}(\mu) P_{\downarrow}(m - \nu). \quad (28)$$

This expression is derived by substituting Eq. (19) into (8) and performing the calculation under the constraint $\mu + \nu = m$. The electron detection probability formulation presented in this section is inherently time dependent, as both the wave function and the region V evolve over time, following the motion of the hydrogen nucleus.

IV. RESULTS AND DISCUSSION

Figure 4(a) presents snapshots from the simulation for hydrogen ion (H^+) incidence in case (b). Initially, the hydrogen ion was positioned far from the tungsten surface, with no electron density surrounding it. At 6.16 fs, electron density transfer from the tungsten surface to the region near the hydrogen nucleus was observed [Fig. 4(b)]. The distance between the hydrogen atom and the tungsten surface was defined as the difference between the initial z coordinate of the first-layer surface and the z coordinate of the hydrogen nucleus at that time. The initial z coordinate of the first-layer surface was calculated as the mean z coordinate of the 12 tungsten atoms comprising the first layer. At this point, the distance between the hydrogen and tungsten surface was 4.59 bohrs, exceeding the typical C-H chemical bond length.

Following the collision of the hydrogen nucleus with a tungsten atom in the second layer, the hydrogen nucleus was reflected and moved away from the surface. Even after it traveled a significant distance from the surface, an electron density remained localized around the hydrogen. Similar electron density transfer was observed in cases (a) and (c). In case (a), the hydrogen ion collided with a tungsten atom in the first layer and was reflected. In contrast, in case (c), the hydrogen ion penetrated the tungsten surface, a result expected due to channeling, a well-known phenomenon in ion beam experiments and simulations.

The detection probability of electrons in the small region V was estimated using Eq. (28). This probability corresponds

to the likelihood of detecting a hydrogen ion in different states: as a positive ion, a neutral atom, or a negative ion. The probability of each state was quantified by defining the small region V as a sphere of radius 6.47 bohrs centered on the hydrogen nucleus. This radius was selected based on a preliminary DFT calculation of an independent hydrogen atom, ensuring that 99.9% of the total electron density was contained within the sphere. Given that tungsten and hydrogen were sufficiently separated, this spherical region provided a reasonable approximation of the hydrogen's region. The total simulation durations for cases (a), (b), and (c) were $t_{\text{end}} = 14.51, 16.93, 19.35$ fs, respectively, with corresponding hydrogen-tungsten distances of 17.17, 15.89, and 16.57 bohrs.

Using the small defined region V , we estimated $P(m)$ ($m = 0, 1, 2$), obtaining the results shown in Fig. 5. The estimated probabilities were approximately 25% for $P(0)$, 50% for $P(1)$, and 25% for $P(2)$. Notably, these values were largely independent of the incident positions (a), (b), and (c).

We investigated how the detection probabilities change when varying the cutoff radius for hydrogen. Figure 6 shows the dependence of the electron detection probabilities on the cutoff radius. From this figure, it can be seen that if the cutoff radius is too small, the electron detection probability is underestimated. In the region where $r_c \leq 3$ bohrs, the probability

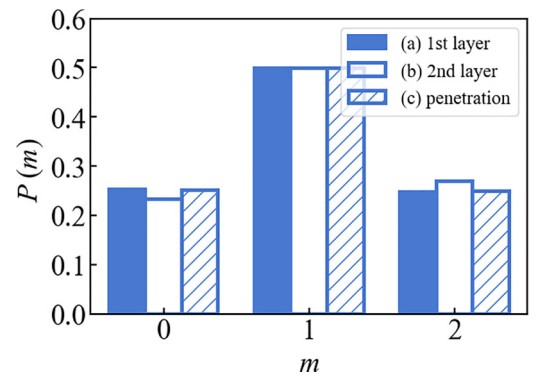


FIG. 5. Detection probability of each state of hydrogen in the final state. The filled, open, and hatched bars show the detection probabilities for incident conditions (a), (b), and (c), respectively.

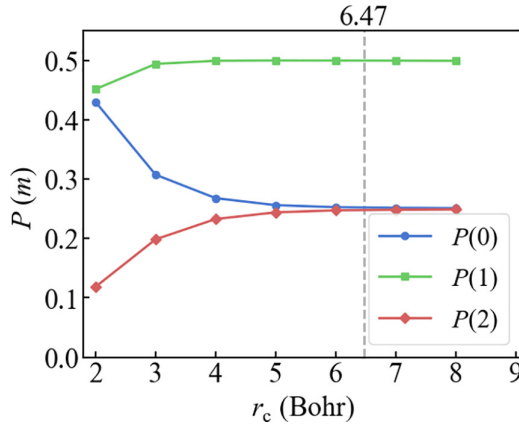


FIG. 6. Dependence of the electron detection probabilities on the cutoff radius for the case of incident condition (a) as defined in Fig. 1.

$P(0)$, which corresponds to no electron being detected around hydrogen, increases, while the probabilities $P(1)$ and $P(2)$, corresponding to the detection of one or two electrons, are underestimated. On the other hand, when the cutoff radius becomes sufficiently large ($r_c \geq 6$), the electron detection probabilities saturate, and $P(0)$, $P(1)$, and $P(2)$ converge to 0.25, 0.5, and 0.25, respectively. These results indicate that the cutoff radius of 6.47 bohrs adopted in this study is appropriate.

The validity of the approximation in Eq. (17) was confirmed by the fact that the maximum value of $\langle \psi_i | \psi_j \rangle_V$ was approximately 0.1. In the analysis presented until now, electron detection probabilities were computed without distinguishing between up-spin and down-spin electrons. Table I presents spin-resolved detection probabilities, computed using Eq. (23). In particular, we examined the components of $P(1) = P(0, 1) + P(1, 0)$, where $P(1, 0)$ and $P(0, 1)$ represent the probabilities of detecting one up electron and one down electron, respectively. The equality of $P(1, 0)$ and $P(0, 1)$ for each incident condition (a), (b), and (c) indicates that spin symmetry was preserved throughout the simulation.

TABLE I. Detection probability of μ -up-spin and ν -down-spin electron as components of $P(m)$. (a), (b), and (c) correspond to the incident conditions.

(a) First layer		
$P(0) = 0.252$	$P(1) = 0.500$	$P(2) = 0.248$
$P(0, 0) = 0.252$	$P(0, 1) = 0.250$	$P(1, 1) = 0.248$
	$P(1, 0) = 0.250$	$P(0, 2) = 2.16 \times 10^{-4}$
		$P(2, 0) = 2.16 \times 10^{-4}$
(b) Second layer		
$P(0) = 0.232$	$P(1) = 0.499$	$P(2) = 0.268$
$P(0, 0) = 0.232$	$P(0, 1) = 0.249$	$P(1, 1) = 0.267$
	$P(1, 0) = 0.249$	$P(0, 2) = 3.07 \times 10^{-5}$
		$P(2, 0) = 3.07 \times 10^{-5}$
(c) Penetration		
$P(0) = 0.252$	$P(1) = 0.500$	$P(2) = 0.248$
$P(0, 0) = 0.252$	$P(0, 1) = 0.250$	$P(1, 1) = 0.248$
	$P(1, 0) = 0.250$	$P(0, 2) = 2.45 \times 10^{-4}$
		$P(2, 0) = 2.45 \times 10^{-4}$

As no external magnetic field was applied, the system evolved while maintaining this symmetry.

We also analyzed the components of $P(2) = P(1, 1) + P(0, 2) + P(2, 0)$. Here, $P(1, 1)$ corresponds to the probability of detecting one up-spin and one down-spin electron, while $P(2, 0)$ and $P(0, 2)$ represent the probabilities of detecting two up-spin and two down-spin electrons, respectively. Among these, $P(1, 1)$ dominated, whereas $P(2, 0)$ and $P(0, 2)$ were minor. This result aligns with the expected electronic configuration of the ground-state hydrogen negative ion, where one up-spin and one down-spin electron occupy the $1s$ orbital. Furthermore, from the perspective of spin symmetry, the small values of $P(2, 0)$ and $P(0, 2)$ were anticipated.

A widely accepted traditional picture of hydrogen ion neutralization is that an electron in a certain surface state transitions to a level around the hydrogen nucleus. Our TDDFT simulations, however, revealed a more detailed mechanism as follows.

As shown in Fig. 4, while the electron density initially exists only around the tungsten atoms, it begins to appear around the hydrogen nucleus as it approaches the surface. This electron density around the hydrogen nucleus is not formed from a single TDKS orbital, but rather from multiple TDKS orbitals. This finding is consistent with the present result that the probability $P(m)$ of detecting more than one electron around the hydrogen nucleus is significant.

To further analyze this behavior, we prepared Fig. 7. In this figure, we selected three of the TDKS orbitals that have transitioned from the tungsten side to the vicinity of the hydrogen nucleus and plotted their amplitudes $|\psi_i(x)|$. Even when focusing on a single orbital among these, a portion of it moves away together with the hydrogen nucleus, while the rest remains near the tungsten atoms. Namely, the TDKS orbitals appear to behave as if they are spatially fragmented. It should be noted, however, that this behavior is predicted by Ehrenfest MD and may differ from the fully quantum-mechanical description of the ideal physical process.

Furthermore, all TDKS orbitals shown in Fig. 7 were initially delocalized over the entire tungsten surface. This observation suggests that weakly bound conduction electrons near the Fermi level contribute to the neutralization process. This observation reinforces the requirement to compute electron detection probabilities from TDKS orbitals to estimate neutralization probability accurately. Conversely, a semiclassical approach might suggest that it suffices to analyze electron density and charge distribution around the hydrogen nucleus. To compare these approaches, we evaluated the electric charge surrounding the hydrogen nucleus using two different definitions. The first approach defines the charge within a simple spherical region V centered on the hydrogen nucleus as

$$Q_S = \int_V dr \rho(r), \quad (29)$$

where V is the same spherical region of radius 6.47 bohrs used in the probability calculations. This definition provides a reasonable estimation of the electronic charge around the hydrogen nucleus when it is sufficiently distant from the surface. However, when the hydrogen nucleus is close to the tungsten

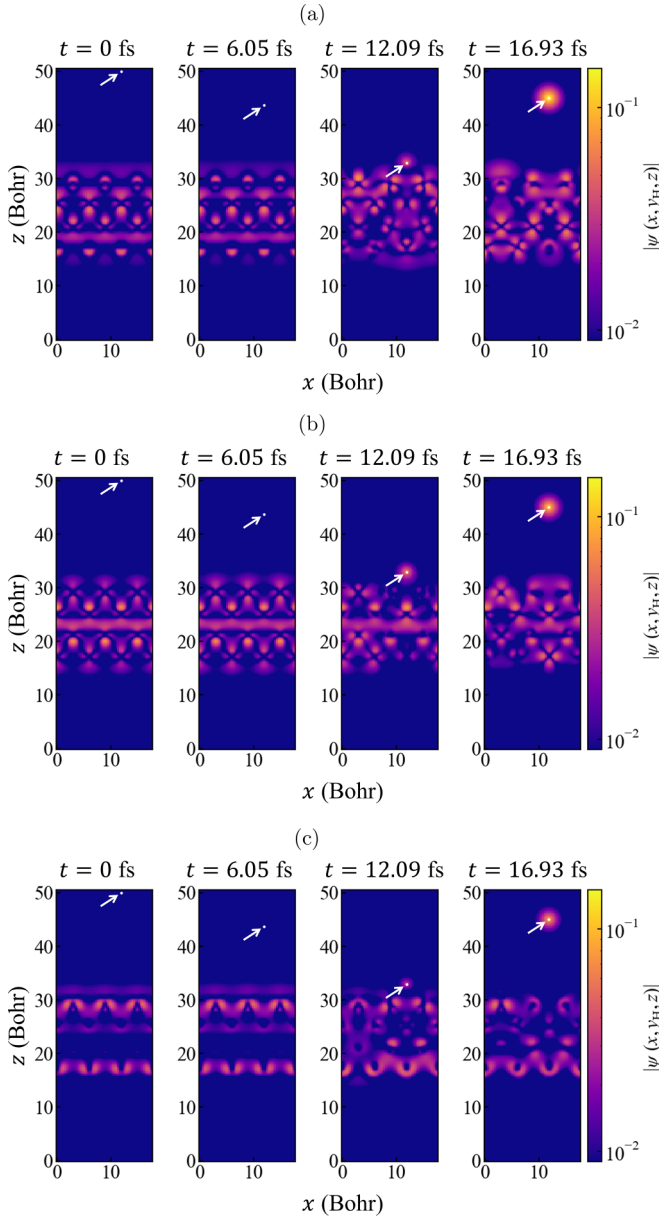


FIG. 7. Time evolution of the absolute values of TDKS orbitals $|\psi_i(x, y_H, z)|$ with indices (a) $i = 46$, (b) $i = 39$, and (c) $i = 190$. Each panel shows a cross section parallel to the xz plane at $y = y_H = 12.67$ bohrs, which includes the hydrogen nucleus.

surface, V overlaps with the tungsten atoms, rendering this definition less reliable.

The second approach employs the Bader charge Q_B [22], which represents the electronic charge within the Bader volume. In contrast to the spherical volume, the Bader volume dynamically deforms over time in response to nuclear motion and is computed using the algorithm proposed by Henkelman *et al.* [23]. The Bader volume provides a more reasonable representation of the charge around the hydrogen nucleus when it is near the tungsten surface. However, when the hydrogen nucleus moves far from the surface, even free electrons in the vacuum region may be included due to the definition of the Bader volume.

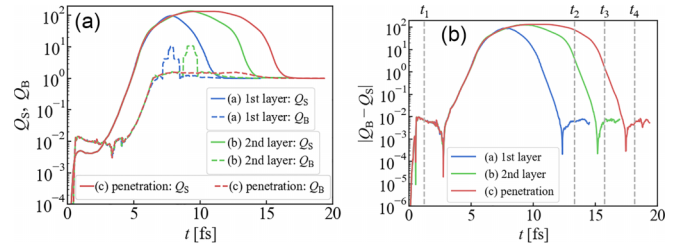


FIG. 8. Time evolution of (a) the charge defined by two methods, Q_B and Q_S , around the hydrogen nucleus, and (b) the absolute difference between Q_B and Q_S . In both panels, the blue, green, and red lines indicate incident conditions (a), (b), and (c), respectively, as defined in Fig. 1.

The time evolution of Q_S and Q_B is shown in Fig. 8(a). From around $t \approx 2.76$ fs onward, a region appears where Q_S becomes greater than Q_B . For instance, in the case of incident condition (a), Q_S remained higher than Q_B until approximately $t \approx 12.3$ fs, with its peak value exceeding 100 electrons. This result suggests that Q_S overestimates the charge around the hydrogen nucleus due to the overlap between V and the tungsten surface.

From Fig. 8(b), the absolute difference between Q_S and Q_B is sufficiently small for $t \approx 2.76$ fs and for the later times $t \approx 12.3$ fs, $t \approx 15$ fs, and $t \approx 17.5$ fs in cases (a), (b), and (c), respectively. During these periods, the hydrogen-surface distance was sufficiently large. Although free electrons are typically included in the Bader charge, the consistency between the two charge definitions after reflection and penetration suggests that free-electron emission due to collisions was negligible under the given simulation conditions. However, when the hydrogen nucleus approached a tungsten atom, the Bader charge became unreliable in cases (a) and (b), with its peak value exceeding 10 electrons. This issue arises due to the nature of the Bader volume definition, which partitions space based on electron density local minima. When the hydrogen nucleus is very close to a tungsten nucleus, a local minimum electron density point may not form between the nuclei, causing a breakdown in the Bader volume definition. This breakdown is observed in the present case due to the 100-eV incident energy and the head-on collision in cases (a) and (b). In contrast, in case (c), where no head-on collision occurred, the Bader charge remained approximately 1–2 electrons.

Ultimately, for all cases (a), (b), and (c), both Q_S and Q_B converge to a value of 1 electron in the final state. However, we hypothesize that a hydrogen atom is not necessarily neutral simply because its charge is 1. Notably, Q_S and Q_B do not represent classical electronic charges. Instead, they correspond to the expected number of electrons in a given volume. The expectation value of the number of electrons, $\langle m \rangle$ detected in V , can be estimated from the detection probabilities $P(m)$. $\langle m \rangle$ is analytically derived to be consistent with the spatial integral of the electron density $\rho(r)$ within V :

$$\langle m \rangle = \sum_{m=0}^n m P(m) = \int_V dr \rho(r) = Q_S. \quad (30)$$

TABLE II. Comparison of the calculated expected number of electrons detected in V and the charge in V . (a), (b), and (c) correspond to the incident conditions. The t_1 through t_4 match those shown in Fig. 8(b). The t_{end} is the final time of the simulation. At these times, there is sufficient separation between the hydrogen and the tungsten surface.

(a) First layer			
Time (fs)	Q_s	$\langle m \rangle$	$ Q_s - \langle m \rangle /Q_s$
$t_1 = 1.21$	0.004568203	0.004568237	7.5357×10^{-6}
$t_2 = 13.30$	0.995181957	0.995180406	1.55919×10^{-6}
$t_{\text{end}} = 14.51$	0.996775713	0.99677447	1.24706×10^{-6}
(b) Second layer			
Time (fs)	Q_s	$\langle m \rangle$	$ Q_s - \langle m \rangle /Q_s$
$t_1 = 1.21$	0.004553505	0.004553467	8.52245×10^{-6}
$t_3 = 15.72$	1.038443954	1.038439063	4.71018×10^{-6}
$t_{\text{end}} = 16.93$	1.037278984	1.037275812	3.05798×10^{-6}
(c) Penetration			
Time (fs)	Q_s	$\langle m \rangle$	$ Q_s - \langle m \rangle /Q_s$
$t_1 = 1.21$	0.00455589	0.004555187	0.000154346
$t_4 = 18.14$	0.99791393	0.997909176	4.76399×10^{-6}
$t_{\text{end}} = 19.35$	0.997539039	0.997537187	1.85644×10^{-6}

A comparison of Q_s and $\langle m \rangle$ is presented in Table II, where V is defined as a spherical region of radius 6.47 bohrs. In this estimation, $\langle m \rangle$ was approximated up to $n = 3$ as $\sum_{m=0}^3 mP(m)$, with $P(m)$ estimated using Eq. (17). The estimates in Table II correspond to a region where the hydrogen nucleus is sufficiently far away from the tungsten surface. In this condition, $\langle m \rangle$ and Q_s agree closely, satisfying Eq. (30). This result confirms that Q_s does not represent a classical charge but an expectation value of the number of detected electrons. Consequently, in TDDFT, it is more appropriate to compute the neutralization probability from TDKS orbitals rather than infer it from electron density. Notably, when Q_s is large, the approximation in Eq. (17) becomes invalid due to the increasing contribution of higher-order terms.

Next, we focus on negative ion formation. Experimental studies have reported negative ion generation on metal surfaces [24–27]. In particular, when the backscattered energy is relatively low, the yield of negative ions on Au surfaces can exceed that of positive ions [28,29]. However, previous theoretical models [5–8] have not accounted for negative ion formation on surfaces.

A key limitation of these previous models is that they do not consider electron spin. In contrast, our spin-polarized TDDFT simulations demonstrated the formation of both neutral atoms and negative ions. In a non-spin-polarized simple DFT (or TDDFT) framework, single-electron detection probabilities cannot be defined because the occupation number for each Kohn-Sham orbital is fixed at 2. By employing spin-polarized TDDFT, we successfully computed a quantum state in which positive ions, neutral atoms, and negative ions coexist.

The probability of negative hydrogen ion formation was found to be significant, as indicated in Fig. 5 and Table I. In our simulation, the tungsten surface was assumed to be ideal

and clean. Because the surface initially exhibited spin symmetry, this symmetry was preserved throughout the simulation, potentially leading to an overestimation of negative hydrogen detection probability.

In real experimental environments, negative ions undergo decay processes. In particular, negative hydrogen ions are readily neutralized via interactions with other particles. However, in our simulations, the system contained only the tungsten target and the incident hydrogen ion, precluding any decay mechanisms. Hence, direct comparisons between this study and experimental observations require caution.

In this study, no significant differences were observed in the final electronic states of hydrogen or in the detection probabilities $P(m)$ among the different incident positions (a), (b), and (c). In cases (a) and (b), head-on collisions occur, resulting in very short distances between the nuclei, whereas in the channeling case (c), the distance between the nuclei remains relatively large. Therefore, in the former cases, core-electron excitation could potentially occur; however, in the present calculations, this may have been suppressed due to the use of pseudopotentials. For reference, although a direct comparison is not possible due to differences in energy range and target material, it has been reported that the use of pseudopotentials in simulations of high-energy proton impacts into a silicon target at 1 MeV or below leads to an underestimation of electronic stopping power [30]. In that context, it has been suggested that part of the electronic stopping originates from core-electron excitation. In this study, the number of valence electrons for tungsten was set to 12; however, it should be noted that using a pseudopotential with a larger number of valence electrons in the future may lead to different behavior in head-on collisions.

In the present calculations, due to limitations in computational resources, the small system size may have introduced finite-size effects. In particular, we are concerned about the limited surface area in the x - y directions. Because of the small surface area and the use of periodic boundary conditions, the number density of incident hydrogen ions per unit area becomes unrealistically high. As a result, a very strong electric field, generated by the bare nuclear charge of hydrogen, may exist above the tungsten surface. This strong electric field could influence the transport of electrons. In future studies, it will be essential to examine the dependence on surface area by performing calculations with larger surface models.

While Ehrenfest MD cannot rigorously describe dynamics involving nonadiabatic branching, we consider it to be appropriate for this study. This is because the hydrogen nuclei are injected perpendicularly onto the tungsten surface, and either reflect vertically or channel through the surface in a nearly straight path. Additionally, the incident energy (100 eV) is sufficiently high to prevent adsorption, and the resulting trajectory branching is expected to be limited. The RT-TDDFT approach used here is implemented on a real-space grid, and the Kohn-Sham orbitals are treated independently of the nuclear coordinates, allowing for a reasonable description of electronic excitations. Surface-hopping-type methods [31–34] may be useful in systems with stronger trajectory branching, but are less suited to the dense excitation spectrum and grid-based framework of this study. Furthermore, Ehrenfest MD enables us to estimate the detection probabilities of pos-

itive, neutral, and negative hydrogen species from a single trajectory with low computational cost. This feature is particularly advantageous for future comparisons with experiments, and we expect that broader sampling over incident positions will be feasible in future studies.

V. CONCLUSION

The neutralization process of a hydrogen ion on tungsten surfaces has long been a fundamental issue in PMI research. To address this, we performed TDDFT simulations to capture the quantum transition dynamics of electron wave functions. Additionally, we proposed a method to evaluate the detection probabilities of electrons surrounding a hydrogen nucleus. Our results demonstrate that, following a collision with the tungsten surface, the reflected hydrogen exists in a superposition of three states: a positive ion, a neutral atom, or a negative ion.

For a hydrogen ion incident at 100 eV on the tungsten (110) surface, the probability of detecting the hydrogen as a neutral atom was approximately 50%. In contrast, the probability of detecting it as a negative ion was approximately 25%.

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Y.T. conceived the project, performed the main TDDFT simulations, and proposed the analysis method. A.M.I. developed the TDDFT code. Y.T. wrote the original draft of the manuscript. A.T. and A.M.I. reviewed and edited the manuscript.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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