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Quantum theory of positronium formation at surfaces

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A quantum-mechanical theory of positronium formation at surfaces is presented. The neutralization probability of positrons implanted into solids escaping from a surface is calculated. The theory of the resonant neutralization of ions at a surface is improved for positrons by taking into account the quantum effect of the motion of the positrons near the surface. The angular distributions and the energy distributions of the emitted positronium are calculated. We give the relationship of the positronium energy distribution and the density of states at the surface.

I. INTRODUCTION

It has recently been recognized that low-energy positron beams provide a powerful probe for analyzing the surfaces of solids.[1,2] Various characteristics of positrons, such as their positive charge, their light mass, and their ability to annihilate and emit gamma rays, enable us to obtain information concerning surfaces which cannot be obtained by other methods using electrons, ions, and photons.

The main purpose of the present paper is to develop a theory of positronium (Ps) formation at surfaces and to show how the electron density of states at surfaces can be extracted from the positronium (Ps) energy distribution. The history of a positron implanted into solids can be divided into three stages; its thermalization, its diffusion, and its annihilation. In the process of thermalization, the energy of the positron is reduced to the thermal energy due to inelastic scattering from electrons and phonons. During the process of diffusion, positrons at the surface escape spontaneously if the work function of the positron is negative. The surface-emitted positrons possess an interesting property qualitatively different from a low-energy electron beam, namely, the formation of a positron atom or positronium. In this paper, we discuss the problem of the formation of the positronium (Ps) flux out of a surface. Since the electron-positron bound state does not exist in an electron gas of the density corresponding to that of real metals,[3,4] Ps formation occurs only outwards from the surfaces of metals. We will recall how the measurement of the Ps flux provides a tool in order to characterize the surface. Here, we investigate theoretically the formation of the positronium out of a surface.

The elementary process of Ps formation has been discussed by various authors, in analogy with the ion-neutralization problem. Nieminen and Oliver[5] discussed Ps formation using the formula of Bloss and Hone,[6-8] which was originally derived for the ion-neutralization probability. In this way, however, the mass of the positron is assumed to be infinite and the quantum recoil effect is ignored. Recently, one of the present authors[9] improved this theory to take into account the quantum recoil effect. Nevertheless the motions of the positron and of Ps were assumed to follow classical trajectories.

The purpose of the present paper is to describe Ps formation in terms of the wave function of the motion of Ps instead of the previously used classical trajectories. Instead of the semiclassical time-dependent Anderson-Newns Hamiltonian, we describe the neutralization problem by using the optical-potential method.[10] Our quantum approach is a quantum-mechanical extension of the semiclassical theory developed for the ion-neutralization problem. The angular distributions and energy distributions of the emitted positronium (Ps) are calculated using this theory. The relation between the energy distribution of the Ps and the surface density of states is discussed.

II. ANGULAR AND ENERGY DISTRIBUTION OF Ps EMITTED FROM SURFACES

Positronium formation is described here using the two-step model, where the escape process of the positron from the surface and the positronium formation process are separately discussed. When the positron's work function from the surface is negative (this is the case for almost all metals), the escape probability of positrons impinging at the surface is unity, from the classical mechanic point of view, and the kinetic energy of the escape positron is the negative value of the positron work function ($-\phi_p$), if the temperature of the solid is not too high.

It is well known that there are two mechanisms allowing the electron exchange between surfaces and adparticles, namely the Auger process and the resonant process. In the case of positronium formation, the resonant process is dominant because the energy level of the positronium is located inside the surface band. Then the probability of positronium formation at a surface is given by the golden-rule formula[11] for resonant charge exchange. In the first Born approximation, it becomes

$$P=(2\pi/\hbar)\sum_{\mathbf{k}}\sum_{m}N(e_{\mathbf{k}})\,|\langle f\langle a\,|\,V\,|\,k\rangle i\rangle\,|^2 \times\delta((-\phi_p)+e_{\mathbf{k}}-E_f-e_a)\ . \tag{1}$$

In this formula, e_a represents an energy level of the positronium associated with the wave function $|\,a\,\rangle$; E_f is the kinetic energy of the emitted positronium from the surface; the wave function of the positronium is denoted by $|\,f\,\rangle$; $e_{\mathbf{k}}$ is the energy of an electron at the surface; ϕ_p is the positron work function; $|\,k\,\rangle$, $|\,i\,\rangle$ represent the initial states of the electron and positron, respectively. This first Born approximation can be improved by taking into account the optical-potential effect in the wave function describing the motion of the positronium, which will be done in the next section.

V in Eq. (1) is the Coulomb interaction between the positron and the electron:

$$V=-e^2/(\,|\,\mathbf{r}_e-\mathbf{r}_p\,|\,)\ , \tag{2}$$

where $\mathbf{r}_e$ and $\mathbf{r}_p$ denote the coordinates of the electron and the positron, respectively. In Eq. (1), N is the Fermi-Dirac distribution function

$$N(e_{\mathbf{k}})=[1+\exp(\phi_e+e_{\mathbf{k}})/k_BT]^{-1}\ , \tag{3}$$

where T is the temperature of the solid, k_B the Boltzmann constant, and ϕ_e is the electron work function.

The calculation of Eq. (1) is, in principal, possible if every wave function is known. However, since little is known about the electron's and the positron's wave functions at a surface, we assume that the matrix elements $\langle f\langle a\,|\,V\,|\,\mathbf{k}\rangle i\rangle$ factorize in the following way:

$$\begin{gathered}\langle f\langle a\,|\,V\,|\,\mathbf{k}\rangle i\rangle=V_{a\mathbf{k}}u_{fi}\ ,\\ V_{a\mathbf{k}}=\langle a\,|\,V\,|\,\mathbf{k}\rangle,\quad u_{fi}=\langle f\,|\,u\,|\,i\rangle\ ,\end{gathered} \tag{4}$$

in order to facilitate the theoretical description.

An equivalent assumption was used in theories of the ion-neutralization based on the Anderson model.[6-8] Thus we can split the matrix element of the positronium formation into that of the inner degrees of freedom and into the motion of the center of mass. After the theoretical investigation of the many-body problems of positrons in metals,[3,4] positronium formation can occur only outwards of a surface since the stable positronium state does not exist inside metals. The density of electrons decreases out from the surface, and we assume a surface exponential decrease

$$u(\mathbf{R})=\exp(-\alpha Z)\theta(Z)\ , \tag{5}$$

where $\mathbf{R}$ is the coordinate of the center of mass of the positron and the electron $\mathbf{R}=(\mathbf{r}_e+\mathbf{r}_p)/2$, and Z is the normal component; we assumed that the solid is located at $Z<0$ and $Z>0$ corresponds to the vacuum region.

From the above-mentioned assumptions, the transition probability P of Eq. (1) can be rewritten as

$$P=(2/\hbar)\int de\,N(e)\Delta(e)\sum_{f}|\,u_{\mathrm{if}}\,|^2\delta((-\phi_p)+e-E_f-e_a)\ . \tag{6}$$

$\Delta(e)$ appears in Newn's theory[12] of chemisorption and represents the lifetime broadening of the atomic level at surfaces

$$\Delta(e)=\pi\sum_{\mathbf{k}}|\,V_{a\mathbf{k}}\,|^2\delta(e-e_{\mathbf{k}})\ , \tag{7}$$

$N(e)$ was defined in (3). Let us explicitly write the sum over f in Eq. (6) as

$$\sum_{f}=V_0\int dP_{f_x}/(2\pi)\int dP_{f_y}/(2\pi)\int dP_{f_\perp}/(2\pi)\ ,$$

where V_0 is a normalization volume element and $\mathbf{P}_f$ is the center-of-mass momentum of Ps. By using now the normal-momentum integral to eliminate the energy δ function

$$\int dP_{f_\perp}\delta(E-(\hbar P_{f_\perp})^2/(2M))=M/(P_\perp\hbar^2)\ ,$$

where M is the mass of the positronium, i.e., twice the electron mass $M=2m$ and $P_\perp=(2ME\cos^2\theta/\hbar^2)^{1/2}$, and by transforming the transverse momentum integration into the external angle of emission, θ, measured from the surface normal

$$\int dP_{f_x}\int dP_{f_y}=\int(2M/\hbar^2)E_f\cos\theta d\Omega\ ,$$

we obtain

$$\sum_{f}|\,u_{fi}\,|^2\delta((-\phi_p)+e-E_f-e_a)=\int dE/(2\pi)V_0\int d\Omega\delta((-\phi_p)+e-E-e_a)\,|\,u_{\mathbf{P}}\,|^2(M/\hbar^2P_\perp)(2\pi)^{-2}[2ME\cos(\theta)/\hbar^2]\ , \tag{8}$$

where $P_\perp$ is the normal component of the positronium's momentum and $u_{\mathbf{P}}=\langle\mathbf{P}\,|\,u\,|\,i\rangle$. Thus, the total transition probability P can be expressed as an integral over energy and solid angle of the differential probability $d^2P/dEd\Omega$:

$$P=\int dE\int d\Omega(d^2P/dE\,d\Omega)\ ,$$

where

$$\begin{aligned}d^2P/(dE\,d\Omega)=V_0(2/\hbar)N(\phi_p+e_a+E)\Delta(\phi_p+e_a+E)\\ \times|\,u_{\mathbf{P}}\,|^2[M/(2\pi\hbar^2P_\perp)]\\ \times[2ME\cos(\theta)/(2\pi\hbar)^2]\ .\end{aligned} \tag{9}$$

Now, we rewrite Eq. (9) using the fact that $u(\mathbf{R})$ in Eq. (5) depends only on the normal coordinate Z, which yields

$$|u_{\mathbf{P}}|^2 = |u_{P_\perp}|^2 (2\pi)^2 S_0 \delta^2(k_\parallel - P_\parallel) V_0^{-2} ,$$

where S_0 is the normalization area of the surface electron and S_0^{-1} is the surface electron density.

Here, it is assumed that the conserved momentum parallel to the surface of the positronium corresponds to that of the sole surface electron; this assumption is valid only if the positronium work function is much larger than $k_B T$ (so that the corresponding component of the positron momentum is negligible), and if the surface is flat enough. By introducing the functions $N_{\mathbf{P}_\parallel}(e)$ and $\Delta_{\mathbf{P}_\parallel}(e)$ taking into account this momentum conservation

$$N(e)\Delta(e)\delta^2(\mathbf{k}_\parallel - \mathbf{P}_\parallel)(2\pi)^2 S_0^{-1} = N_{\mathbf{P}_\parallel}(e)\Delta_{\mathbf{P}_\parallel}(e) \tag{10}$$

we rewrite Eq. (9) as

$$\begin{aligned} d^2P/dE\,d\Omega = {} & V_0^{-1} S_0^2 (2/\hbar) N_{\mathbf{P}_\parallel}(e_a + E + \phi_p) \\ & \times \Delta_{\mathbf{P}_\parallel}(e_a + E + \phi_p) |u_{P_\perp}|^2 [M/(2\pi\hbar^2 P_\perp)] \\ & \times [2ME\cos\theta/(2\pi\hbar)^2] . \end{aligned} \tag{11}$$

By normalizing this by the initial flux of the center of mass of the relevant positron and the electron, $(v_i S_0/V_0)$, we obtain the angular and the energy resolved neutralization probability as follows:

$$\begin{aligned} d^2n/dE\,d\Omega = {} & S_0 (2/\hbar v_i) N_{\mathbf{P}_\parallel}(e_a + E + \phi_p) \\ & \times \Delta_{\mathbf{P}_\parallel}(e_a + E + \phi_p) |u_{P_\perp}|^2 \\ & \times [M/(2\pi\hbar^2 P_\perp)][2ME\cos\theta(2\pi\hbar)^{-2}] , \end{aligned} \tag{12}$$

where $v_i = |2(-\phi_p)/M|^{1/2}$ because there is no electron flux from the surface into the vacuum. It is noted that the direction of the positron escaping out of a flat surface is perpendicular to it.

Now, let us examine each term of the right-hand side of Eq. (11). First we discuss the parallel momentum fixed Fermi-Dirac distribution function $N_{\mathbf{P}_\parallel}$. For the solid of the absolute zero temperature

$$N_{\mathbf{P}_\parallel}(e_a + E + \phi_p) = 0$$

when

$$E > -\phi_p - e_a - \phi_e .$$

Then, the emitted positronium energy is restricted such as

$$E \langle -\phi_{\mathrm{Ps}} ,$$

where ϕ_{Ps} is the positronium work function defined by

$$\phi_{\mathrm{Ps}} = e_a + \phi_e + \phi_p .$$

In the case of the free-electron model, we may calculate the integration of $N_{\mathbf{P}_\parallel}(e_a + E + \phi_p)$ over $P_\perp$ as

$$\int dP_\perp N_{\mathbf{P}_\parallel}(e_a + E + \phi_p) = |k_F^2 - P_\parallel^2|^{1/2} ,$$

where k_F is the Fermi momentum. The energy cutoff created by the Fermi-function will be sensitive in the angular distribution of the positronium flux, if the condition

$$(-\phi_{\mathrm{Ps}}) > (\hbar k_F)^2/2M$$

is satisfied. However, the positronium work function ϕ_{Ps} is much smaller than the Fermi energy for almost all real metals. Therefore $N_{\mathbf{P}_\parallel}(e)$ is nearly constant with respect to the emission angle θ.

Now, we discuss the structure of Eq. (11) arising from the $\Delta_{\mathbf{P}_\parallel}$, is defined by

$$\Delta_{\mathbf{P}_\parallel}(e_a + E + \phi_p) = \sum_{\mathbf{k}} |V_{a\mathbf{k}}|^2 \delta(e_a + E + \phi_p - e_k)|_{\mathbf{k}_\parallel = \mathbf{P}_\parallel} .$$

When the matrix element $V_{a\mathbf{k}}$ is a constant with respect to k, this becomes

$$\Delta_{\mathbf{P}_\parallel}(e_a + E + \phi_p) = |V_a|^2 \rho_{\mathbf{P}_\parallel}(e_a + E + \phi_p) , \tag{13}$$

where $\rho_{\mathbf{P}_\parallel}$ is the parallel momentum fixed surface density of states. Then the surface density of states is proportional to the energy distribution of the positronium flux.

This presents us with a method for measuring the electronic structure of surfaces which has some advantages in comparison with other methods such as photoemission or Auger emission spectroscopy.[13] First, positronium formation occurs outwards from the surface, that is, positrons pick up the electrons from the sole surface. Then the energy distribution of the positronium represents the electronic density of states at surfaces, $\mathbf{k}_\parallel$ resolved or integrated, according to the experimental set up. Second, it is not necessary to consider the effect of the final electron density of states. The final-state effects do not appear in the positronium kinetic-energy distribution because the final electron state is a well-defined bound state of the positronium and no longer an electronic state. For an electron emission method such as photoemission, the electron current involves the final electronic states, which makes it a difficult task to extract the initial density of states from the measured spectrum of the electron current. Therefore we have shown that it is possible to determine the surface density of states directly, from the precise measurement of the kinetic-energy distribution of the emitted positronium.

We can also represent Eq. (12) in terms of the perpendicular and normal energy variables $(E_\perp = E\cos^2\theta)$, which are used by Mills *et al.*[14] to describe the time-of-flight experiments. According to the relation

$$d^2n/dE\,d\Omega = (E\cos\theta/\pi) d^2n/dE_\perp dE_\parallel$$

the normal energy distribution of the positronium $dn/dE_\perp$ becomes

$$dn/dE_\perp = (2/\hbar v_i)(1/E_\parallel^0) \int dE_\parallel N_{\mathbf{P}_\parallel}(e_a + E_\perp + E_\parallel + \phi_p) \Delta_{\mathbf{P}_\parallel}(e_a + E_\perp + E_\parallel + \phi_p) |u_{P_\perp}|^2 (1/2\pi\hbar) |2M/\hbar^2 E_\perp|^{1/2} , \tag{14}$$

where $E_\parallel^0 = (2\pi\hbar^2/MS_0)$ is an upper limit of $E_\parallel$. The upper limit of the integration over $E_\parallel$ in Eq. (14) is also affected by the geometrical condition of the measurement. The acceptance half angle of the detector is denoted as γ. In the case of the wide band limit, where $\Delta_{\mathbf{P}_\parallel}(e)$ is independent of e and $\mathbf{P}_\parallel$, the result of the integration of the right-hand side of Eq. (15) becomes

$$\begin{aligned}(1/E_\parallel^0)\int dE_\parallel N_{\mathbf{P}_\parallel}(e_a+E_\perp+E_\parallel+\phi_p)=&\,\theta(-\phi_{\mathrm{Ps}}-E_\perp-E_\parallel^0)\theta(E_\perp\tan^2\delta-E_\parallel^0)\\&+(E_\perp\tan^2\gamma/E_\parallel^0)\theta(-\phi_{\mathrm{Ps}}-E_\perp\sec^2\gamma)\theta(-E_\perp\tan^2\gamma+E_\parallel^0)\\&+[(-\phi_{\mathrm{Ps}}-E_\perp)/E_\parallel^0]\theta(\phi_{\mathrm{Ps}}+E_\perp\sec^2\gamma)\theta(\phi_{\mathrm{Ps}}+E_\perp+E_\parallel^0)\ . \end{aligned}\tag{15}$$

When $E_\parallel^0$ is larger than ϕ_{Ps}, this expression is equivalent to that of Mills *et al.*,[14] which explains well their experiments. In fact, the structure of the normal energy distribution of formed positrons $dn/dE_\perp$ is dominated by the one-dimensional free particle density of state associated with the motion of the positronium out of the surface and by the geometrical condition of the measurements given by Eq. (15) if the initial electron density effect appearing in Δ and the transition matrix effect u of Eq. (14) can be ignored. However the effect of $|u_{P_\perp}|^2$ cannot be neglected in the structure of $dn/dE_\perp$ of Eq. (14), which is discussed in Sec. III.

III. OPTICAL-POTENTIAL METHOD

The motion of the center of mass of the positron and electron out of the surface is assumed to be described by a plane wave, which is a solution of the Schrödinger equation for free particles

$$\left[-\left[\hbar\frac{d}{dZ}\right]^2\Big/(2M)\right]|P_\perp\rangle=E_\perp|P_\perp\rangle\ .$$

In the first Born approximation, $|u_{P_\perp}|^2$ is calculated as

$$\begin{aligned}|u_{p_\perp}|^2&=\left|\int_0^\infty dZ\exp(-iP_iZ)\exp(-\alpha Z)\exp(iP_\perp Z)\right|^2\\&=|(P_i-P_\perp)^2+\alpha^2|^{-1}\ .\end{aligned}\tag{16}$$

Let us examine the contribution of this factor to the structure of $dn/dE_\perp$ of Eq. (14) using the typical value of α, P_i, and $P_\perp$. Since the attenuation length of electrons from the surface is about 1 Å, α is 0.5 (a.u.). The value of the positron work function is about 0.01 (a.u.) and P_i $[=2M(-\phi_p)/\hbar^2]^{1/2}$ is 0.2 (a.u.). The positronium work function is 0.1 (a.u.). Then $P_\perp$ varies from 0 to 0.7 (a.u.). Therefore $|u_{P_\perp}|^2$ of Eq. (16) varies by a factor of 2 in the typical range of measured $P_\perp$. This variation is important for the energy distribution of the positronium. However the calculation based on the Born approximation is not sufficient for the quantitative purpose.

The validity of the Born approximation is examined by calculating the total positronium formation probability. If Δ is constant and if the positronium work function is infinite, the total positronium formation probability n is given by

$$n=\Delta/\hbar v\alpha(\equiv\xi)\ .\tag{17}$$

Since Δ is of the order of 0.1 a.u., this quantity exceeds unity; this indicates that the Born approximation is appropriate for treating the positronium formation probability.

The optical-potential method has been introduced in order to describe the charge exchange scattering of atoms at surfaces by one of the present authors.[10] We will extend it here to the positronium formation. The optical potential due to the electron exchange between the ion (or positron) and the solid, W, is added to the Schrödinger equation for the wave function describing the motion of the center of mass of the positron and the electron as follows:

$$\left[-\left[\hbar\frac{d}{dZ}\right]^2/(2M)+W\right]|P_\perp\rangle^W=E|P_\perp\rangle^W\ ,\tag{18}$$

where $|P_\perp\rangle^W$ is the modified wave function taking into account the optical potential. The Born approximation of Eqs. (1) and (16) can be modified[15] by using $|P_\perp\rangle^W$ instead of $|P_\perp\rangle$:

$$|u_{P_\perp}|^2=|{}^W\langle P_\perp|u|P_i\rangle|^2\ .\tag{19}$$

The optical potential W due to the resonant charge exchange is given by[10]

$$\begin{aligned}W&=\sum_{f'}\sum_{\mathbf{k}}\frac{u|f'\rangle\langle f'|u}{E+e_a-e_{\mathbf{k}}-E_{f'}+i\delta}|V_{a\mathbf{k}}|^2\\&=\sum_{f'}\int de\frac{1}{\pi}\Delta(e)\frac{u|f'\rangle\langle f'|u}{E+e_a-e-E_{f'}+i\delta}\ .\end{aligned}\tag{20}$$

We show here that the optical-potential method for the neutralization probability, Eq. (20), is a generalization of the time-dependent Anderson-Newns model method, which has been widely used for the ion-neutralization problem,[6-8] in order to take into account the quantum effect of the motion of the atoms (or positrons). The scattering T matrix is written in terms of the optical potential as[15]

$$T=V+WG_0T\ ,\tag{21}$$

where

$$G_0=\left[-\left[\hbar\frac{d}{dZ}\right]^2(2M)-E\right]^{-1}\ .$$

We note that

$$^{W}\langle P_\perp \langle a \mid V \mid k \rangle i \rangle = \langle P_\perp \langle a \mid \mathbf{T} \mid \mathbf{k} \rangle \mathrm{i} \rangle$$

and $\langle P \langle a \mid V \mid \mathbf{k} \rangle i \rangle$ is given by Eq. (1). The time-evolution operator $U(t)$ is given as the integration of the T matrix in the interaction picture.

$$U = 1 - (i/\hbar) \int_{-\infty}^{t} dt' T^{I}(t') \ . \tag{22}$$

The matrix element of U satisfies the following integro-differential equation:

$$\begin{aligned} \dot{U}_{ak} &= -(i/\hbar) T^{I}_{a\mathbf{k}}(t) = -(i/\hbar) \left[V_{a\mathbf{k}} u^{I}(t) - \int_{-\infty}^{t} W^{I}(t,t') U_{a\mathbf{k}}(t') dt' \right] \\ &= -(i/\hbar) \left[V_{a\mathbf{k}} u^{I}(t) - (i/\pi\hbar) \int de\, \Delta(e) \int_{-\infty}^{t} dt' \exp[-i(e - e_a)(t-t')] u^{I}(t) u^{I}(t') U_{ak}(t') \right] . \end{aligned} \tag{23}$$

If $u^{I}(t)$ is the classical c-number function of time such as $u^{I}(t) = u[Z(t)]$ [where $Z(t)$ represents a classical trajectory], this integro-differential equation is nothing but the equation obtained from the time-dependent Anderson-Newns model[16] in the limit of the one-electron theory. Therefore our optical-potential approach is a quantum-mechanical extension of the semiclassical trajectory approximation using the time dependent model. It is noted that the equation (23) is difficult to solve even by numerical methods because u^{I} is an operator. Then we will present several approximations for $\mid P_\perp \rangle^{W}$.

A. WKB approximation

The optical-potential given by Eq. (20), which is nonlocal in general, becomes a local imaginary potential in the case of the wide-band limit

$$W = -i \Delta u(Z)^2 \ . \tag{24}$$

The wave function $\mid P_\perp \rangle^{W}$ satisfying Eq. (18) can be calculated with the Wentzel-Kramers-Brillouin (WKB) approximation for the optical potential of (24) as

$$\langle Z \mid P_\perp \rangle^{W} = \exp(iP_\perp Z) \exp \left[- \int_{Z}^{\infty} dZ' u(Z')^2 M\Delta/\hbar^2 P_\perp \right] = \exp(iP_\perp Z) \exp[-\exp(-2\alpha Z) M\Delta/(2\hbar^2 P_\perp \alpha)] \ . \tag{25}$$

Using this wave function, $u_{P_\perp}$ can be calculated by

$$u_{P_\perp} = \int_{0}^{\infty} dZ \exp[i(P_\perp - P_i)Z] \exp(-\alpha Z) \exp[-\exp(-2\alpha Z)\xi_f/2] \ , \tag{26}$$

where $\xi_f = \Delta M/\hbar^2 P_\perp \alpha$. Two approximations are introduced to facilitate the integration of Eq. (26). The first one is the Bloss and Hone[6-8] approximation, which is obtained by changing the variable Z of Eq. (26) into $\eta = \exp(-2\alpha Z)\xi_f/2$,

$$u_{P_\perp} = \frac{1}{2\alpha} \int_{0}^{\xi_{f/2}} d\eta/\eta \exp[-\eta](2\eta/\xi_f)^{[\frac{1}{2} + i(P_i - P_\perp)/(2\alpha)]} \ . \tag{27}$$

If the upper limit of the integration of (27) ξ_f is replaced by infinity, the result becomes

$$u_{P_\perp} = (1/2\alpha)\Gamma[\tfrac{1}{2} + i(P_i - P_\perp)/(2\alpha)](2\xi_f)^{-[\frac{1}{2} + i(P_i - P_\perp)/(2\alpha)]} \ ,$$

where Γ is the Gamma function. Substituting back into Eq. (14), we obtain the total neutralization probability n:

$$n = (\tfrac{1}{2}\hbar v_i \alpha) \int dE\, N(e_a + E + \phi_p) \operatorname{sech}[\pi(P_\perp - P_i)/(2\alpha)] \ . \tag{28}$$

This result is equivalent to that originally obtained by Blandin *et al.*,[6] Bloss and Hone,[7] and Brako and Newns[8] for the ion-neutralization problem. In fact, since the value of ξ_f is much larger than unity for the charge exchange of slow atoms (ions), near surfaces, the domain of validity of this formula for the neutralization probability is broad. On the other hand, Niemminen and Oliva[5] and one of the present authors[9] applied equation 28 to positronium formation. However the assumption of $\xi_f \rightarrow \infty$, which is valid for the slow ion-neutralization problem, fails for positronium formation because ξ_f is of order of unity. The second approximation of Eq. (26) is the rate-equation approximation, where $\mid u_{P_\perp} \mid^2$ is calculated as

$$\begin{aligned} \mid u_{P_\perp} \mid^2 &= \int_{0}^{\infty} dZ \int_{-Z}^{Z} dZ' \exp \mid -i(P_i - P_\perp)Z' \mid \exp \left[- \int_{Z+(Z'/2)}^{\infty} dZ'' \alpha \xi_f \exp(-2\alpha Z'') \right] \\ &\qquad \times \exp \left[- \int_{Z-(Z'/Z)}^{\infty} dZ'' \alpha \xi_f \exp(-2\alpha Z'') \right] \exp(-2\alpha Z) \\ &\cong \int_{0}^{\infty} dZ \exp(-2\alpha Z) \exp[-\xi_f \exp(-2\alpha Z)] 2 \sin[(P_i - P_\perp)Z]/(P_i - P_\perp) \ . \end{aligned} \tag{29}$$

When the positronium work function ϕ_{Ps} is infinite and Δ is constant, the total neutralization probability n is obtained from Eq. (29) as

$$n = N(e_a)[1-\exp(-\xi)] \ . \tag{30}$$

This result is identical to the rate equation in the ion-neutralization problem.[17] At any rate these two approximate solutions of Eq. (26) (both of which being used to discuss the ion neutralization probability at surface) cannot be appropriate for the quantitative discussion of the neutralization probability of positrons. In Fig. 1 we compare $|u_{P_\perp}|^2$ obtained from the direct calculation of Eq. (26), the Bloss-Hone–type approximation of Eq. (28), and the rate equation approximation of Eq. (29).

B. Normalized Born approximation

This approximation has been proposed by one of the present authors to describe the ion-neutralization probability using the optical-potential method.[10] According to this, the wave function $|P\rangle^W$ is written by

$$\langle Z \mid P_\perp \rangle^W = \exp(iP_\perp Z)[1+i\langle P_\perp \mid W \mid P_\perp \rangle M/(2\hbar^2 P_\perp)]^{-1} \ , \tag{31}$$

where $\langle P_\perp \mid W \mid P_\perp \rangle$ is the diagonal matrix element of the optical potential W, which is calculated in the wide-band limit

$$\langle P_\perp \mid W \mid P_\perp \rangle = \sum_{f'} (1/\pi) \int de\, \Delta(e) \frac{|\langle P_\perp \mid u \mid f' \rangle|^2}{E+e_a-e-E_{f'}+i\delta}$$
$$= -(i\Delta/2\alpha)[\tfrac{1}{2}+(1/\pi)\tan^{-1}(P_\perp/\alpha)] \ . \tag{32}$$

By using Eq. (31), $|u_{P_\perp}|^2$ becomes

$$|u_{P_\perp}|^2 = \frac{1}{|(P_\perp-P_i)^2+\alpha^2|} \times \frac{1}{|1+i\langle P_\perp \mid W \mid P_\perp \rangle M/(2\hbar^2 P_\perp)|^2} \ . \tag{33}$$

This approximation is valid when ξ_f is of order of unity, which is the condition of positronium formation. In fact, the WKB approximation of Sec. III A cannot be applied for the narrow-band case where the nonlocality of the optical potential becomes important. On the other hand, the normalized Born approximation, which does not require the assumption of the locality of the optical potential, is appropriate for the narrow-band case. Therefore, this method may be useful to analyze the energy distribution of the positronium formed at surfaces.

In Fig. 1, we show the calculation of $|u_{P_\perp}|^2$ using the normalized Born approximation of Eq. (33). It should be emphasized that the WKB and the normalized Born approximations give quite close results in the wide-band limiting case. The Born approximation, which may be better in the region of large $P_\perp$, gives too large a value of $|u_{P_\perp}|^2$. The two approximations introduced for the ion neutralization, the Bloss-Hone–type of Eq. (28) and the rate equation of Eq. (29), are not appropriate for the positronium formation. Figure 2 shows the Ps energy distribution, $dn/dE_\perp$ for an Al(111) surface. The collimator's open-angle γ of Eq. (15) is chosen as $(\pi/2)$. The Born and the normalized Born approximations are used for the

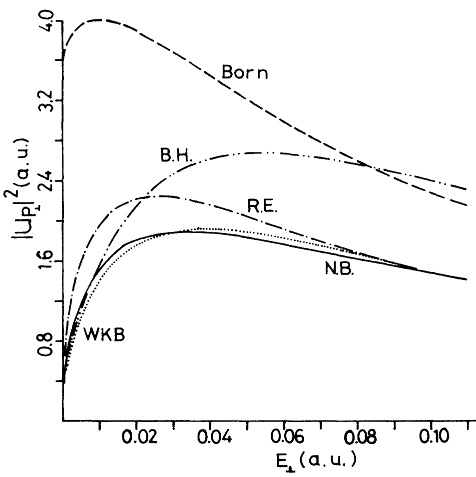

FIG. 1. $|u_{P_\perp}|^2$ as a function of $E_\perp[=(\hbar P_\perp)^2/(2M)]$. The parameters are $\phi_{\text{Ps}}=-0.1$ a.u., $\phi_p=0.01$ a.u., $\Delta=0.2$ a.u., and $\alpha=0,5$ a.u.. Dashed line corresponds to the Born approximation [Eq. (16)], dotted line to the WKB approximation [Eq. (26)], double-dotted-dashed line to the Bloss-Hone approximation [Eq. (28)], dotted-dashed line to the rate equation approximation [Eq. (29)], and solid line to the normalized Born approximation [Eq. (33)], respectively.

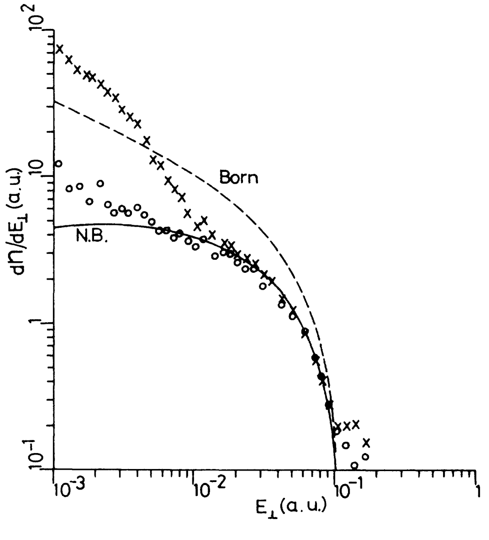

FIG. 2. Normal energy distribution of the formed positroniums $dn/dE_\perp$. Solid and dashed lines are calculated using the normalized Born and Born approximation, respectively. The parameters are the same for Fig. 1. Total escaped positronium yield n is calculated as 0.165 from the normalized Born and 0.40 from the Born approximations, respectively. Experimental energy spectra of the positronium emitted from Al(111) surface by Mills and Pfeiffer (Ref. 18) are marked by × and ○, for temperatures 692 K and 303 K, respectively.

calculation. This calculation is compared with the experimental Ps energy spectra of Fig. 3 of Ref. 18. A qualitative agreement is obtained between our calculation and the temperature independent (or high-energy) part of the experimental spectra. This indicates that the change of $\Delta(e)$ with respect to the energy is not so important in this restricted energy range near the Fermi level. However knowledge of the surface density of states is needed for quantitative comparison with experiment.

We note that the calculated spectra in the low-energy region is proportional to $1/E_\perp$ using the Born approximation and is constant using the normalized Born approximation. The temperature-independent part of the experimental spectra is constant in the low-energy region, which suggests the effectiveness of the normalized Born approximation. This can be confirmed from the recently measured two-dimensional momentum distributions of Ps emitted from surfaces by Howell *et al.*[19] and Lynn *et al.*,[20] which agree well with calculations based on the normalized Born approximation.[21]

IV. CONCLUDING REMARKS

In this paper, we described theory of the positronium formation probability at surfaces using quantum perturbation theory. The energy and angular distribution of the positronium was calculated. It was shown that the Born approximation poorly describes the positronium formation. We presented an optical-potential method for this problem, which constitutes an improvement to the Born approximation for positronium formation probability below unity. It was also demonstrated that our optical-potential method is a quantum extension of the semiclassical time-dependent Anderson-Newns theory for the ion-neutralization problem. Contrary to the classical trajectory approximation, which cannot be used for the positronium formation, and also to the Born approximation, which cannot be applied to this problem, our quantum theory including the multiple charge exchange process in the form of the optical potential seems to be appropriate for the experimental analysis.

In our approach, the energy level of the positronium, e_a, is assumed to be constant with respect to the distance from the surface. However, the image potential acts on the positronium to shift the energy level as a function of the distance from the surface. This effect is handled in the semiclassical theory of ion neutralization by introducing the time-dependent energy level $e_a(t)$.[22] Nevertheless, this cannot be applied to our quantum theory, where time does not appear explicitly.

The optical-potential formalism provides a solution for our problem. It is well known that the optical potential for charged particles due to the surface-plasmon excitation turns out the image potential in the low velocity limit, that is,

$$W^{\text{surface plasmon}} = -(e^2\hbar w_s/2)\int_0^\infty dq\,\exp(-2qZ)/[\hbar w_s + (\hbar q)^2/2M] \cong -e^2/4Z\ ,$$

where w_s is the surface-plasmon frequency. Thus, using the Schrödinger equation with an optical potential describing the surface plasmon, we are able to take into account the image potential.

Now, we point out several fundamental problems in the theory of the positronium formation at surfaces. In our present theory, a two-step model of the positronium formation is applied. The first step is the escape of positrons out of the surface and the second step is positronium formation in the vacuum. We handle the first step classically; thus the escape probability of positrons is assumed to be unity if the positron work function is negative. In our description of the second step, the wave function of center of mass of electron and positron describes the state in the vacuum region. However, in this theory it is not possible to describe the positronium formation at the surfaces for a positive positron work function. Experimentally,[23] the existence of Ps formation at these surfaces has been pointed out.

A one-step model describing the positronium formation where the escape of the positron and the positronium formation are simultaneously taken into account may be adequate in both cases. However the quantum one-step model for the positronium formation contains a fundamental difficulty, even for the negative work function case, that the calculated escape probability of the positron from the surface for a negative work function decreases as a function of the temperature and approaches zero as the temperature becomes zero. The transmission intensity of positrons through the surface is

$$t = 4P_0P_i/[(P_0+P_i)^2] \simeq 4[k_BT/(-\phi_p)]^{1/2}\ ,$$

where $P_0^2/(2m) = k_BT$ is the kinetic energy of the positron inside the solid and $P_i^2 - P_0^2 = 2m(-\phi_p)$. This temperature dependence does not agree with the experimental fact that the temperature dependence of the transmission intensity is minor.[24] This descrepancy of the transmission intensity between theory and experiment exists also for the "transmission problem" of the sticking probability of neutral gas atoms at surfaces, which remains unsolved till now.[15] Further theoretical study is needed for the one-step model of the positronium formation to overcome the difficulty of the "transmission problem."

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[1] J. B. Pendry, in *Positron Solid State Physics*, edited by W. Brandt and A. Dupasquier (North-Holland, New York, 1983).

[2] P. J. Schultz, K. G. Lynn, and W. E. Frieze, in Proceedings of the International Workshop on Slow Positrons in Surface Science, 1983 [Helsinki University of Technology, Report No. 134, 1984 (unpublished)].

[3] A. Held and S. Kahana, Can. J. Phys. **42**, (1964) 1908.

[4] H. Kanazawa, Y. H. Ohtsuki, and S. Yanagawa, Phys. Rev. **138**, A1155 (1965).

[5] R. M. Nieminen and J. Oliva, Phys. Rev. B **22**, 2226 (1980).

[6] A. Blandin, A. Nourtier, and D. W. Hone, J. Phys. (Paris) **37**, 369 (1976).

[7] W. Bloss and D. W. Hone, Surf. Sci. **72**, 253 (1978).

[8] R. Brako and D. M. Newns, Surf. Sci. **108**, 253 (1981).

[9] A. Isii, Surf. Sci. **147**, 227 (1984); **147**, 295 (1984).

[10] S. Shindo and R. Kawai, Surf. Sci. **165**, 477 (1986).

[11] J. W. Gadzuk, Surf. Sci. **6**, 133 (1967); **6**, 159 (1967).

[12] D. M. Newns, Phys. Rev. **178**, 1123 (1969).

[13] B. Feuerbacher and R. F. Willis, J. Phys. C. **9**, 169 (1976).

[14] A. P. Mills, Jr., L. Pfeiffer, and P. M. Platzmann, Phys. Rev. Lett. **51**, 1085 (1983).

[15] S. Shindo, Surface Sci. **159**, 283 (1985).

[16] K. L. Sebastian, V. C. Jyothi, and T. R. Grimley, Surf. Sci. **110**, L571 (1981).

[17] R. Kawai, Phys. Rev. B **32**, 1031 (1986).

[18] A. P. Mills, Jr. and L. Pfeiffer, Phys. Rev. B **32**, 53 (1985).

[19] R. H. Howell, P. Meyer, I. J. Rosenberg, and M. J. Flass, Phys. Rev. Lett. **54**, 1698 (1985).

[20] K. G. Lynn, A. P. Mills, Jr, R. N. West, S. Berko, K. Canter, and L. O. Roelling, Phys. Lett. **54**, 1702 (1985).

[21] S. Shindo and A. Ishii, Phys. Rev. B (to be published).

[22] J. K. Nørskov and B. I. Lundqvist, Phys. Rev. B **19**, 5661 (1979).

[23] K. G. Lynn and D. O. Welch, Phys. Rev. B **22**, 99 (1980).

[24] P. J. Schultz and K. G. Lynn, Phys. Rev. B **26**, 2390 (1982).