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Physical processes in positronium formation at metal surfaces

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The rate of positronium formation (pickup) near a metal surface undergoing bombardment with medium energy positrons is calculated within an approximate model. The formation process proceeds in three stages: slowdown (during which the positron is thermalized due to inelastic positron–conduction-electron and positron-phonon scattering), diffusion (which brings the positron from the characteristic stopping distance to the surface), and electron capture (which takes place at the surface). The process is formulated in terms of a phenomenological Boltzmann-equation approach. We then calculate the range and the microscopic features of the positron diffusion. It is shown that the thermal positron may be regarded as undergoing an isotropic random walk. The role of the surface potential in impeding the positronium formation is discussed and a picture evolves of the positron making several attempts at tunneling through the *attractive* surface barrier before escaping with a captured electron. Our final results for the pickup fraction are in reasonable qualitative agreement with recent experimental results of Mills.

I. INTRODUCTION

We present results of a study of the recently observed high conversion efficiency of positrons into positronium (Ps) atoms occurring at a metal surface upon which a medium-energy positron beam is impinging (pickup). Recent experimental results obtained by Mills[1] for Al indicate remarkably high conversion efficiencies of as much as 75% for incident positron energies of ~ 1 keV. The intent of our calculation is to account qualitatively for this general aspect of very high conversion efficiencies at medium energies. The pickup process at medium energies is shown to proceed via the following stages[2]: (we take the positron normally incident and with energy of the order of $\sim 10^2 - \sim 10^4$ eV). As a result of inelastic scattering by plasmons, electron-hole pairs, and phonons, the positron slows down to thermal velocities (thermalization) in a time generally much shorter than the annihilation lifetime (provided the metal temperature is not too low). By the time the positron has thermalized it will have penetrated to a characteristic distance of $\sim 10^3 - 10^5$ a.u. from the metal surface. (This penetration distance is greatly limited by the strong randomizing effect on the direction of the positron velocity due to the positron–conduction-electron scattering.[3]) The positron then will undergo a thermal random walk as a result of interaction primarily with phonons and will with a certain probability (which involves the penetration depth and microscopic characteristics of the random walk) reach the surface prior to annihilation. There, in the low electron density tail region it will have the opportunity to capture an electron and leave the metal as Ps. The Ps formation almost certainly takes place in the surface region since Ps is believed not to exist in bulk (e.g., Callaway[4]). We note that electron capture is a much more energetically favorable process than either bare positron escape or positron retention in the metal. It is therefore not implausible that capture is very likely once the positron has reached the surface. In that case the pickup fraction is determined primarily by the slow down and diffusion processes.

An integral equation for the pickup fraction is obtained which formally incorporates the effect of the positron inelastic scattering within the metal, positron surface barrier scattering, and the (phenomenological) surface capture probability. Though the solution of the integral equation was not attempted for reasons of time limitation we elaborate on the ideas discussed above in Secs. III–V, considering in an independent way the three stages of the process described above. First principles results on the stopping and diffusion stages are presented. Positron–conduction-electron and positron-phonon scattering are taken into account. We examine the microscopic characteristics of the diffusion and show that the thermal positron may be regarded as undergoing an isotropic random walk. This fact is used to obtain an expression for the number of positrons which diffuse to the surface from the characteristic stopping distance prior to annihilation. We then elucidate the role of the surface barrier in impeding the appearance of Ps in the vacuum. Finally, the strong likelihood of electron capture by a positron near the surface is argued. Our conclusions lead to a result for the pickup fraction for Al in the medium-energy range which is in qualitative agreement with experiment (Sec. VI).

II. FORMULATION IN TERMS OF A PHENOMENOLOGICAL BOLTZMANN EQUATION

We obtain a general formal expression for the yield of Ps atoms which leave a metal surface upon which a monoenergetic beam of positrons is incident. This is done in the context of a dynamically responding jellium model for the metal. Taking the metal surface parallel to the $x=0$ plane, we at this stage make the approximation that the real part of the effective (optical) potential, $\Sigma_R(\vec{v},\vec{r})$, is a constant Σ_0 independent of velocity $\vec{v}$ and position $\vec{r}$ for $x>0$, and zero for $x<0$:

$$\Sigma_R(\vec{v},\vec{r})=\Sigma_0\theta(x) \quad (1a)$$

We furthermore take the imaginary part of the effective potential, $\Sigma_I(\vec{v},\vec{r})$, to be of the form

$$\Sigma_I(\vec{v},\vec{r})=\Sigma_I(\vec{v},x)\theta(x) \ ; \quad (1b)$$

i.e., inelastic scattering occurs only for $x>0$. Note that the actual Σ_R will differ from Eq. (1a) in having a long-range image potential contribution Σ_i and a short-range surface layer contribution Σ_s (both tending asymptotically to zero). Neglect of Σ_s is justifiable since there are present in the system high-energy positrons (which do not see the total effective barrier in any case) and very low-energy (thermal) positrons and Ps atoms whose wavelengths are much larger than the scale of variation of Σ_s. Moreover, Σ_i is not important for the high-energy positron beam nor for the neutral Ps atoms in the vacuum. The effect of Σ_i on thermal positrons may however be important and we allow for its inclusion at a later stage. The assumption of velocity independence of Σ_R is justified since most of the positron distribution in the metal will be concentrated in the thermal energy range within which the electronic screening of the positron is essentially velocity independent.[5]

We begin by considering the distribution function $f(\vec{v},\vec{r},t)$ for positrons, ignoring for the moment the possibility of positronium formation. The positronium fraction will be eventually related to f. The Boltzmann equation (BE) for f has the general form

$$-\vec{v}\cdot\vec{\nabla}_{\vec{r}}f(\vec{v},\vec{r},t)-\frac{\vec{F}(\vec{r})}{m}\cdot\vec{\nabla}_{\vec{v}}f(\vec{v},\vec{r},t)$$
$$+\int[M(\vec{r},\vec{v},\vec{v}')f(\vec{v}',\vec{r},t)$$
$$-M(\vec{r},\vec{v}',\vec{v})f(\vec{v},\vec{r},t)]d^3v'$$
$$-\frac{1}{\tau}f(\vec{v},\vec{r},t)=\frac{d}{dt}f(\vec{v},\vec{r},t) \ , \quad (2)$$

where m is the positron mass, $\vec{F}$ is an external force, and $M(\vec{r},\vec{v},\vec{v}')$ is the differential transition probability from $\vec{v}'\rightarrow\vec{v}$ per unit time. The last term on the left-hand side of Eq. (2) is a sink term describing positron annihilation with τ being the relaxation time for annihilation. We are interested in steady state solutions and therefore equate the left-hand side of Eq. (2) to zero.

In our model [Eq. (1)] there is translational invariance parallel to the interface and thus f can only depend upon $v=|\vec{v}|$, $\mu=\vec{v}\cdot\hat{x}/v$, and x:

$$f(\vec{v},\vec{r})=f(v,\mu,x) \ . \quad (3)$$

Moreover, we may exploit the fact that all space can be divided into two regions ($x<0$ and $x>0$), each of which has distinct physical properties, and solve two separate BE's. We then match solutions at the boundary at $x=0$ in such a way as to incorporate the important effect (see below) of quantum mechanical reflection at the surface.

Assuming that the number of positrons in the system is sufficiently low that we may neglect positron-positron interaction and noting that for $x<0$ there is no external force, no annihilation, and no collisional mechanism, the positron distribution function for $x<0$, $f_1(v,\mu,x)$, satisfies

$$-v\mu\frac{d}{dx}f_1(v,\mu,x)=0 \ . \quad (4)$$

From Eq. (4) f_1 can only depend on v and μ and may be written as (exhibiting the incident beam)

$$f_1(v,\mu)=\delta(v-v_0)\delta(\mu-1)+f_{1s}(v,\mu) \ , \quad (5)$$

where $v_0\hat{x}$ is the beam velocity and where $f_{1s}(v,\mu)$ is the scattered distribution leaving the surface. $f_{1s}(v,\mu)$ is nonzero only for negative μ.

Once $f_{1s}(v,\mu)$ is determined, the total Ps pickup fraction $P(v_0)$ will be taken as proportional to the velocity integral of a phenomenological velocity dependent fraction, $\rho(v,\mu)$, of the flux [$\sim f_{1s}(v,\mu)$] of positrons just outside and leaving the surface:

$$P\sim\int_0^\infty dv\int_{-1}^0 d\mu\rho(v,\mu)f_{1s}(v,\mu) \ . \quad (6)$$

$\rho(v,\mu)$ is obtained by analyzing the microscopic capture process operative at the surface.

In order to obtain $f_{1s}(v,\mu)$ we must obviously solve the BE for the distribution $f_2(v,\mu,x)$ inside the metal. $f_2(v,\mu,x)$ satisfies

$$-v\mu\frac{d}{dx}f_2(v,\mu,x)$$
$$+\int[M(v,\mu,\vec{v}')f_2(v',\mu',x)$$
$$-M(\vec{v}',v,\mu)f_2(v,\mu,x)]d^3v'$$
$$-\frac{1}{\tau_A}f_2(v,\mu,x)=0, \quad x>0 \ . \quad (7)$$

$M(\vec{v},\vec{v}')$ is the position independent differential transition rate arising from, e.g., positron–conduction-electron and positron-phonon interaction. τ_A is the bulk positron annihilation lifetime. We solve Eq. (7) with a boundary condition at the vacuum-metal interface which takes account of the quantum mechanical reflection of a positron approaching the step barrier [Eq. (1)] from within the metal. We note that the effective barrier is typically $\sim 0.1-0.3$ eV.[6] Now we will be concerned with temperatures $\sim 300-\sim 1000$ K for which thermal energies are ~ 0.01 eV. As this is small compared to the barrier, a thermal positron approaching the surface is subject to strong quantum effects. Since it is the thermal positrons that are of central importance in pickup it is clear that we must take account of the quantum mechanical reflection. We thus impose the boundary conditions: ($+\mu$ denotes positive μ, etc.)

$$f_2(v,+\mu,0)=R(v\mu)f_2(v,-\mu,0)+T(v\mu)\delta(v-v_0')\delta(\mu-1) \quad , \quad (8)$$

where $R(v\mu)$ is the reflection coefficient of a positron of normal velocity $v\mu$ incident upon the barrier from the right and where $T(v\mu)$ is the transmission coefficient of a positron of normal velocity $v\mu$ just inside the metal and which entered from the vacuum with normal velocity $v'\mu'=[(v\mu)^2+(2/m)\Sigma_0]^{1/2}$. We emphasize that $R(v\mu)$ is at this point arbitrary and may therefore be chosen to correspond to a potential barrier having an image potential contribution. The last term in Eq. (8) corresponds to the incident beam of velocity $v_0=[v_0'^2+(2/m)\Sigma_0]^{1/2}\hat{x}$ in the vacuum. In addition to the condition Eq. (8), we must require that

$$f_2(v,+\mu,L)=f_2(v,-\mu,L)\rightarrow 0, \quad L\rightarrow\infty \quad . \quad (9)$$

Once having solved for $f_2(v,\mu,x)$ we determine $f_{1s}(v,\mu)$ using

$$f_{1s}(v',-\mu',0)=\bar{T}(v\mu)f_2(v,-\mu,0) \quad , \quad (10)$$

where $v'=[v^2+(2/m)\Sigma_0]^{1/2}$, $\mu'=[(v\mu)^2+(2/m)\Sigma_0]^{1/2}/v'$, and where $\bar{T}(v\mu)$ is the transmission coefficient of a positron of normal velocity $v\mu$ in the metal incident upon the barrier from the right. What Eq. (10) does in effect is to relate the flux at a given velocity vector in the metal to the flux at the corresponding *refracted* velocity vector in the vacuum via the quantum mechanical transmission probability.

An integral equation for f_2 is now obtained. From Eq. (7)

$$\frac{d}{dx}f_2(v,\mu,x)+\alpha(v,\mu)f_2(v,\mu,x)=\frac{1}{v\mu}\int M(v,\mu,\vec{v}')f_2(v',\mu',x)d^3v' \quad , \quad (11)$$

where

$$\alpha(v,\mu)=\frac{1}{v\mu}\left[\int M(\vec{v}',v,\mu)d^3v'+\frac{1}{\tau_A}\right] \quad . \quad (12)$$

We introduce a particular Green's function $G_p(v,\mu,x,x')$ which satisfies

$$\frac{d}{dx}G_p(v,\mu,x,x')+\alpha(v,\mu)G_p(v,\mu,x,x')=\delta(x-x') \quad , \quad (13)$$

and which is given by

$$G_p(v,\mu,x,x')=[\theta(\mu)\theta(x-x')-\theta(-\mu)\theta(x'-x)]e^{-\alpha(v,\mu)(x-x')} \quad . \quad (14)$$

We write the most general Green's function,

$$G(v,\mu,x,x')=G_p(v,\mu,x,x')+G_h(v,\mu,x,x') \quad , \quad (15)$$

where $G_h(v,\mu,x,x')$ satisfies the homogeneous equation corresponding to Eq. (11). We note that $G_h(v,\mu,x,x')$ has the form

$$G_h(v,\mu,x,x')=g(v,\mu,x')e^{-\alpha(v,\mu)x} \quad . \quad (16)$$

A formal solution f_{2s} to Eq. (11) may be written in terms of G:

$$f_{2s}(v,\mu,x)=\frac{1}{v\mu}\int G(v,\mu,x,x')M(v,\mu,\vec{v}')\times f_2(v',\mu',x')d^3v'dx' \quad . \quad (17)$$

We require that this formal scattered solution satisfy the condition (9) and the condition (8) without the δ-function term. From Eq. (17) we see that these conditions can be satisfied by choosing G to be such that

$$G(v,+\mu,0,x')M(v,+\mu,\vec{v}')=R(v\mu)G(v,-\mu,0,x')M(v,-\mu,\vec{v}') \quad , \quad (18)$$

$$G(v,+\mu,L,x')M(v,+\mu,\vec{v}')=G(v,-\mu,L,x')M(v,-\mu,\vec{v}'), \quad L\rightarrow\infty \quad . \quad (19)$$

Using Eqs. (14) and (15) in Eqs. (18) and (19) leads to

$$[G_p(v,+\mu,0,x')+g(v,+\mu,x')]M(v,+\mu,\vec{v}')=R(v\mu)[G_p(v,-\mu,0,x')+g(v,-\mu,x')]M(v,-\mu,\vec{v}') \quad , \quad (20)$$

$$[G_p(v,+\mu,L,x')+g(v,+\mu,x')e^{-\alpha(v,+\mu)L}]M(v,+\mu,\vec{v}')=[G_p(v,-\mu,L,x')+g(v,-\mu,x')e^{-\alpha(v,-\mu)L}]M(v,-\mu,\vec{v}'), \quad L\rightarrow\infty \quad . \quad (21)$$

Making use of Eq. (12) and the fact that for a homogeneous system

$$\alpha(v,+\mu) = -\alpha(v,-\mu) \ , \tag{22}$$

we arrive at

$$g(v,-\mu,x') = 0 \ , \tag{23}$$

$$g(v,+\mu,x') = \frac{R(v\mu)e^{-\alpha(v,+\mu)x'}M(v,-\mu,v')}{M(v,+\mu,\vec{v}')}, \quad 0<\mu<1 \ . \tag{24}$$

Thus the desired G is given by

$$G(v,\mu,x,x') = G_p(v,\mu,x,x') + \theta(\mu)\frac{R(v\mu)M(v,-\mu,\vec{v}')e^{-\alpha(v,\mu)(x+x')}}{M(v,+\mu,\vec{v}')} \ . \tag{25}$$

To the particular solution Eq. (17) [with G chosen as Eq. (25)] we add a solution $f_0(v,\mu,x)$ of the homogeneous equation corresponding to Eq. (11) which corresponds to the incident beam, namely,

$$f_0(v,\mu,x) = T(v\mu)\delta(v-v_0)\delta(\mu-1)e^{-\alpha(v,\mu)x} \ . \tag{26}$$

Thus, the desired $f_2(v,\mu,x)$ is given as the solution of the following inhomogeneous Fredholm equation of the second kind and in four variables

$$f_2(v,\mu,x) = T(v\mu)\delta(v-v_0)\delta(\mu-1)e^{-\alpha(v,\mu)x} + \frac{1}{v\mu}\int [G_p(v,\mu,x,x')M(v,\mu,\vec{v}') + \theta(\mu)R(v\mu)M(v,-\mu,\vec{v}')e^{-\alpha(v,\mu)(x+x')}]\, f_2(v',\mu',x')d^3v'dx' \ . \tag{27}$$

We note that the choice of Green's function Eq. (25) guarantees that $f_2(v,\mu,x)$ satisfies the condition Eq. (8). Solution of Eq. (27) gives $f_2(v,-\mu,0)$ which then enables us to compute the pickup fraction $P(v_0)$ via Eqs. (10) and (6).

Though the formulation of this section allows in principle for the solution for the pickup fraction in terms of the functions ρ, R, and M characterizing, respectively, the surface capture probability, the surface reflection, and the bulk inelastic scattering, the actual solution of the Boltzmann equation was not attempted for reasons of time limitation. Rather we have calculated the pickup fraction in accordance with the above picture by considering in turn each of the three stages of the process (stopping, diffusion, and capture) in an independent way.

III. STOPPING

It is first necessary to know the mean depth of penetration (range), R, of a positron entering a metal. For this we take over the result of a previous calculation.[3] There the range is calculated by a recursive scheme which requires as an input only the bulk differential transition probability of the positron in

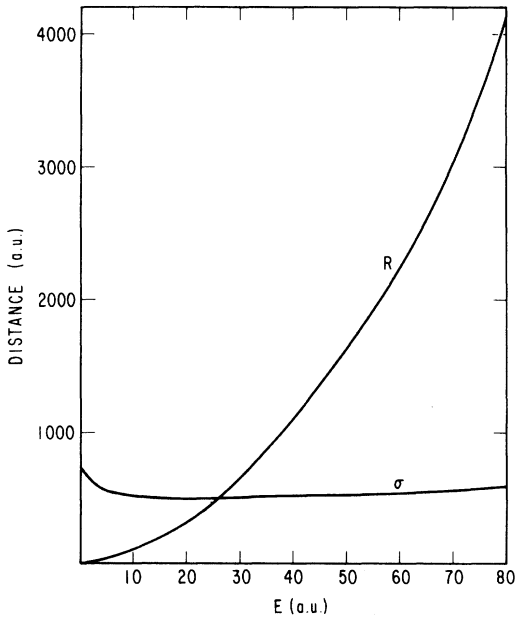

FIG. 1. Range R and its rms deviation σ vs energy for a positron entering Al (from Ref. 3). The intersection at $E \approx 25$ a.u. indicates that most positrons thermalize before returning to the surface for $E \gtrsim 25$ a.u.

the metal. Both conduction-electron and phonon scattering were taken into account. The rms deviation σ, in the range is also given there. The result for Al (which we will concentrate on) is reproduced for convenience in Fig. 1. We see that in the energy range 40–80 a.u., $R \sim 10^3$ a.u. We note that as the energy is increased above ~ 40 a.u., the ratio σ/R rapidly decreases; i.e., the distribution of penetration depths becomes more peaked taking us away from the picture of an exponential distribution as used in Ref. 1.

It is worth mentioning that the result of Fig. 1 indicates that a significant and increasing number of positrons reach the surface before having completely thermalized as E is reduced from ≈ 25 a.u. (note $\sigma > R$ in this energy range). This is in line with the results of Mills, Platzman, and Brown (Ref. 6) on positron emission. It moreover indicates that nonthermalized positrons may play an important role in low-energy pickup since the pickup fraction is found to increase as E is lowered in the range 0–25 a.u.

IV. DIFFUSION

Turning then to the diffusion stage, we now calculate the fraction P of medium energy positrons which, after having thermalized at some characteristic distance from the surface (taken as R), diffuse to the surface prior to annihilation. It is well known[7,8] that for most metals in the temperature range of interest and for positron energies $\sim < 10^2$ a.u., the thermalization time $\tau_{\rm th}$ is a small fraction of the annihilation lifetime τ_A ($\tau_A \sim 10^{-10}$ sec). For Al we have found taking account of both conduction-electron and phonon scattering that for energies $\sim 10^2$ a.u. and temperatures $T = 300$ K (900 K), $\tau_{\rm th} \sim 0.01$ $(\sim 0.002)\tau_A$. Thus the positron spends nearly all of its time during the conversion process undergoing diffusion in thermal equilibrium.

We next indicate the microscopic characteristics of the diffusion, i.e., mean free path and mean scattering angle per collision. It has been shown that at typical thermal energies phonon scattering dominates over conduction-electron scattering[8,9] and that for Al, taking into account the effect of the thermally excited phonons, the mean free path λ at $T = 300$ K (900 K) is $\sim 1.5 \times 10^2$ a.u. ($\sim 9.0 \times 10^1$ a.u.).[10] Thus a positron of energy ~ 50 a.u. stops within ~ 10 (thermal) mean free paths of the surface.

The time rate of change of angular deflection, $\dot{\theta}(p)$ of a positron of momentum p due to phonon scattering in a metal has been shown to be given as[3]

$$\dot{\theta}(p) = \int \sigma_{\rm ph}(\vec{\rm p}, \vec{\rm p} - \vec{\rm k})\theta(\vec{\rm k}) d^3k \quad , \tag{28}$$

where the differential transition rate per unit time due to phonon scattering is given (for a thermal positron) as

$$\sigma_{\rm ph}(\vec{\rm p}, \vec{\rm p} - \vec{\rm k}) = \frac{\gamma^2}{4\pi^2} k\, \delta(E(p) - \omega(k) - E(\vec{\rm p} - \vec{\rm k})) \times \theta(\omega_D - \omega(k)) \quad , \tag{29}$$

where γ is the positron-phonon coupling constant, ω_D is the Debye frequency, $E(p) = p^2/2m$ is the free positron energy, and $\omega(k) = ck$ is the phonon energy where c is the velocity of sound. In Eq. (28), doing first the trivial azimuthal integration and then the $x = \cos\theta_{\vec{\rm k},\vec{\rm p}}$ integration, we then change variables from the magnitude of the momentum transfer $|\vec{\rm k}|$ to the scattering angle

$$\theta(k, x(k)) = \sin^{-1}\left(\frac{k[1 - x(k)^2]^{1/2}}{[p^2 + k^2 - 2pkx(k)]^{1/2}} \right) \quad , \tag{30a}$$

$$x(k) = -\frac{1}{p}\left(\tfrac{1}{2}k + mc\right) \quad . \tag{30b}$$

This leads to, after some algebra,

$$\dot{\theta}_{\rm ph}(E) = \frac{\gamma^2 m^2 \sqrt{2E}}{\pi} \int_0^{\pi} (1 - \cos\theta)^{1/2} \theta \sin\theta \, d\theta,$$

$$\tfrac{1}{2}mc^2 << E << \frac{1}{4}\frac{\omega_D^2}{2mc^2} \quad . \tag{31}$$

Writing the integrand of Eq. (31) as $D(\theta)\theta$, we see that $D(\theta) \sim (1 - \cos\theta)^{1/2}\sin\theta$ is the differential scattering probability into angle θ. Note that $D(\theta) = 0$ for $\theta = 0, \pi$ and has a maximum for $\theta = \cos^{-1}(-\frac{1}{3}) \approx 1.9$ rad. Thus we see that the scattering is primarily at roughly right angles to the original direction of motion at thermal energies.

Thus during the diffusive stage, we have the approximate picture of a positron undergoing a correlated random walk such that at each step it is required to move in a direction $\sim 90°$ from the immediately preceding direction of movement. It is shown in Appendix A that such a correlated random walk is equivalent to an isotropic random walk provided that the total number of steps in not too small.

Now for a medium energy positron $R \sim 10^3$–10^4 a.u. while the thermal $\lambda \sim 10^2$ a.u. (implying thermal collision times $\sim 10^{-3}\tau_A$). Thus all characteristic distances (i.e., range and total path length) are large compared to λ. Therefore, for purposes of computing the number of positrons which diffuse to the surface (regarding the diffusion as a correlated random walk) we may go to the limit of large N (step number) where the correlated random walk is effectively isotropic. For the present we ignore the possible reflection of positrons by the surface and assume that every positron that reaches the surface is removed from the system.

It is shown in Appendix B that given a particle undergoing an isotropic random walk in three dimen-

sions and which was started m step lengths from an absorbing surface, it will have arrived at the surface after a total of $\mathfrak{N}$ collision times with a probability P given by

$$P(\mathfrak{N},m)=\frac{3}{2}\frac{1}{\sqrt{\pi}}\left[m\Gamma\left(-\frac{1}{2},\frac{3m^2}{2\mathfrak{N}}\right)-\frac{1}{3}(m-1)\Gamma\left(-\frac{1}{2},\frac{3(m-1)^2}{2(\mathfrak{N}-1)}\right)-\frac{2}{3}m\Gamma\left(-\frac{1}{2},\frac{3m^2}{2(\mathfrak{N}-1)}\right)\right.$$
$$-\frac{1}{3}m\Gamma\left(-\frac{1}{2},\frac{3}{2}m\right)+\frac{1}{3}(m-1)\Gamma\left(-\frac{1}{2},\frac{3}{2}(m-1)\right)$$
$$\left.-\frac{2}{3}\left[\gamma\left(\frac{1}{2},\frac{3}{2}\mathfrak{N}\right)-\gamma\left(\frac{1}{2},\frac{3}{2}(\mathfrak{N}-1)\right)+\frac{1}{3}\gamma\left(\frac{1}{2},\frac{3}{2}(m-1)\right)-\frac{1}{3}\gamma\left(\frac{1}{2},\frac{3}{2}m\right)\right]\right], \quad (32)$$

where $\Gamma(\alpha,x)$ and $\gamma(\alpha,x)$ are the incomplete gamma functions of the first and second kind

$$\Gamma(\alpha,x)=\int_x^\infty e^{-t}t^{\alpha-1}dt \quad (\mathrm{Re}\,\alpha>0) , \quad (33)$$

$$\gamma(\alpha,x)=\int_0^x e^{-t}t^{\alpha-1}dt . \quad (34)$$

Note that m reflects the range and mean free path while $\mathfrak{N}$ reflects the total path length (i.e., the annihilation lifetime) and mean free path. We return to formula (32) after examining the capture process.

V. CAPTURE

We now examine the electron capture which takes place at the metal surface. Consider a system consisting of a single positron and a $\frac{1}{2}$-space metal having N electrons (N large). We write down three expressions for the fixed total energy of the system. The first expression applies when the positron is in thermal equilibrium within the metal at temperature T:

$$E=E_0(N-1)+\mu_e+\mu_p+E_{\mathrm{th}}(T) , \quad (35)$$

where $E_0(N-1)$ is the equilibrium energy of an $N-1$ electron gas, where μ_e is the chemical potential of an electron, where μ_p is the chemical potential of a positron at $T=0$ and where $E_{\mathrm{th}}(T)$ is the thermal energy of the positron in the metal at temperature T. μ_e and μ_p are measured with respect to the potential energy at an infinite distance from the metal. Therefore μ_e and μ_p are the negatives of the electron and positron work functions.

If the positron is moved (at fixed total energy) to a distance infinitely far outside the metal, the energy may be written as

$$E=K_p+E_0(N-1)+\mu_e+\mathcal{S}(N,\alpha) , \quad (36)$$

where K_p is the kinetic energy of a free positron and where $\mathcal{S}(N,\alpha)$ is the positive excitation energy of an N-electron gas corresponding to the positron's retaining an energy K_p at infinity. The maximum positron kinetic energy $K_{p\max}$ [set $\mathcal{S}(N,\alpha)=0$ in Eq. (36) and equate Eqs. (35) and (36)] is given by

$$K_{p\max}=\mu_p+E_{\mathrm{th}}(T) . \quad (37)$$

[The recent experiments by Mills, Platzman, and Brown[6] on Al indicate $K_{p\max}\approx 0.1$–0.3 eV $\approx\mu_p$ (since $T\sim 300$ K $\Rightarrow E_{\mathrm{th}}\sim 0.01$ eV).] Equation (37) suggests that we may regard the thermal positron as moving in an effective potential $v_p(x)$ which vanishes far oustside the metal and which equals μ_p far inside. Naturally this effective potential must include the image potential which becomes significant near the surface, dropping to a minimum of the order of ~ 10 eV a few Å outside the surface (Fig. 2).

We next move the positron and a single electron far outside the metal and allow them to form Ps in the ground state, all at fixed total energy. The energy is expressed as

$$E=\epsilon_B+K_{\mathrm{Ps}}+E(n-1,0)+\mathcal{S}(N-1,\alpha') , \quad (38)$$

where ϵ_B and K_{Ps} are the internal ground-state energy and translational energy of the Ps atom, respectively. Setting $K_{\mathrm{Ps}}=K_{\mathrm{Ps}\max}$ [$\Rightarrow\mathcal{S}(N-1,\alpha')=0$] and equating Eqs. (35) and (38) we get

$$\mu_p+E_{\mathrm{th}}(T)+\mu_e=\epsilon_B+K_{\mathrm{Ps}\max} . \quad (39)$$

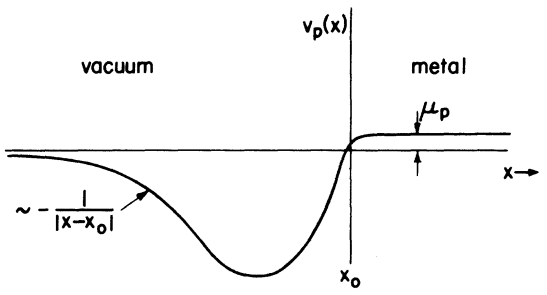

FIG. 2. Effective potential v_p seen by a positron near a metal surface. The image force gives rise to the deep well just outside the surface and to the asymptotic $\sim 1/|x-x_0|$ behavior.

Recall that μ_p is given by

$$\mu_p = V_c + V_d \ , \tag{40}$$

where V_c is the correlation energy and where V_d is the electrostatic dipole barrier.

Let us now take the point of view that the correlation energy V_c is a negative binding energy of a positroniumlike complex. That is, we regard the positron plus its screening cloud as an effective two-body state with internal energy V_c. In general $V_c \neq \epsilon_B$. Given the value for V_d (e.g., Lang and Kohn[11]) we may use Eq. (40) in Eq. (37) to determine V_c in terms of the experimental $K_{p\,\max}$:

$$V_c = K_{p\,\max} - V_d - E_{\rm th}(T) \ . \tag{41}$$

Knowing V_c and defining $\epsilon_B' \equiv V_c$ we are led to

$$\epsilon_B' + V_d + \mu_e + E_{\rm th}(T) = \epsilon_B + K_{\rm Ps\,max} \ . \tag{42}$$

This equation suggests that there is a "positronium atom" with a position dependent coupling constant and which moves in an effective potential $v_{\rm Ps}(x)$ which vanishes in the vacuum and which is equal to $V_d + \mu_e$ in the metal. In the case of Al, ϵ_B' happens to be approximately equal to $\epsilon_B [K_{p\,\max} \sim 0.2$ eV, $V_d \sim 7$ eV $\Rightarrow \epsilon_B' = -7$ eV, $\epsilon_B = -7$ eV (i.e., $\frac{1}{2}$ Ry)]. Thus for Al the positronium atom may be regarded as moving unmodified in the effective potential. Since Ps is neutral there will be no image potential contribution to the effective potential (Fig. 3). For Al, $V_d + \mu_e = +3.0$ eV. Thus the Ps atom is repelled from the interior of the metal.

We have now built up two pictures: one of a positron moving in an effective potential v_p, the other of a Ps-like complex moving in an effective potential $v_{\rm Ps}$. These pictures lead to two extreme points of view in regard to capture. In the first picture, the thermal positron approaches the interface, escapes with a certain probability and then captures the electron with a certain probability. In the second picture the capture has taken place prior to the positron's reaching the surface and the Ps complex escapes, with a certain probability of not being ionized. Naturally the actual mechanism lies somewhere between these two views. Nonetheless we can gain some insight by considering these mechanisms.

Now from the earlier discussion we are able to conclude that the Ps work function[12] for Al, which is given by $-(V_d + \mu_e) \approx -0.3$ eV, is considerably more negative than the bare positron work function $-\mu_p \approx -0.2$ eV; i.e., the tendency of a Ps atom to spontaneously leave the metal is much greater than the same for the bare positron. This is in line with the general conclusions of Hodges and Stott.[13] Since Ps emission is more energetically favored than bare positron emission, we somewhat crudely but not unreasonably assume that every positron which leaves the metal leaves in a Ps atom.

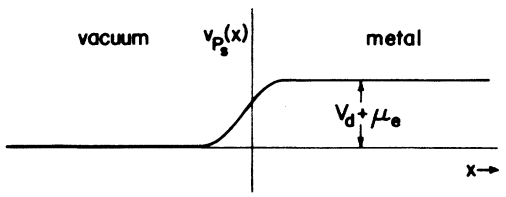

FIG. 3. Effective potential $v_{\rm Ps}$ seen by a positroniumlike complex near a metal surface.

Thus, with this assumption, in the first picture, the capture fraction manifests only the bare positron tunneling probability through the barrier v_p whereas in the second picture it manifests only the Ps-complex tunneling probability over the barrier $v_{\rm Ps}$.

The barrier heights are $V_p \sim 0.2$ eV and $V_{\rm Ps} \sim 3$ eV for Al; in both cases the positron approaches an attractive barrier with the thermal energy $E_{\rm th}(T) \sim \frac{3}{2} k_B T$ which is smaller than even V_p.

Now it is easily shown[14] that the reflection coefficient of a particle approaching an arbitrary attractive steplike barrier of height V tends to unity as its kinetic energy tends to zero. In fact it is generally significantly different from zero for kinetic energies $\sim \frac{1}{4} V$. For example, replacing $v_p(x)$ and $v_{\rm Ps}(x)$ by square step profiles of height V_p and $V_{\rm Ps}$ we find for $T = 300$ K (900 K) reflection coefficients of ~ 0.35 (~ 0.20) and ~ 0.75 (~ 0.65), respectively. Thus the more attractive barrier is more impenetrable. This might suggest in view of the large observed conversion efficiencies that the first model is closer to reality. However, in fact $v_p(x)$ unlike $v_{\rm Ps}(x)$ includes a significant image potential contribution which results in the profile taking a substantial dip of ~ 10 eV just outside the surface. What is more, the drop in $v_p(x)$ outside the surface takes place on a much smaller spatial scale (~ 1–2 Å) than does the rise through the $\sim 1/z$ region toward zero (~ 20 Å), and $v_p(x)$ thus has the local appearance of a large step. In fact, numerical solution of the Schrödinger equation using the Ying, Smith, and Kohn[15] image potential profile gives a reflection coefficient of ~ 0.80 (~ 0.70) for $T = 300$ K (900 K), even higher than that for $v_{\rm Ps}(x)$.

Thus we have reached the unexpected conclusion that the appearance of Ps in the vacuum region is significantly impeded by the *attractive* surface potential. This observation suggests that what in fact occurs at the surface is a succession of attempts by the positron udergoing a thermal random walk to tunnel out. Given a reflection coefficient r and transmission coefficient t the probability of transmission t_n after n attempts is simply

$$t_n = 1 - r^n \ . \tag{43}$$

Therefore in order to realize an effective transmis-

sion coefficient of t' there must be n' attempts, given by

$$n' = \frac{1}{\ln r} \ln(1 - t') \ . \tag{44}$$

For example, with $r = 0.80$, we may realize an effective transmission coefficient of ~ 0.90, say, with ~ 10 attempts.

VI. RESULTS FOR PICKUP FRACTION

We now are in a position to estimate the pickup fraction $f(E,T)$ for incident energy E and temperature T. In Sec. V we suggested that it is not implausible and moreover assume here than any thermal positron escaping through the surface forms Ps. This escape follows a succession of attempts. Thus, a positron near the surface will form Ps with a probability approaching unity after ~ 10 attempts. This number of attempts will roughly correspond to α 10 collision times (τ) where α is a factor of order ~ 10. Since the time the particle spends in attempting to cross the barrier is small compared to the total time τ_A spent undergoing diffusion [$\alpha(10\tau) \sim 10^{-1}\tau_A$] our result for the total escape probability Eq. (32) calculated ignoring the surface reflecion still approximately applies. We thus take

$$f(E,T) = P(\mathfrak{N}, m) \ , \tag{45}$$

where

$$\mathfrak{N} = \frac{\tau_A}{\tau(T)} \tag{46}$$

is the total number of steps before annihilation [$\tau(T)$ being the collision time at temperature T] and where

$$m = \frac{R}{\lambda(T)} \tag{47}$$

is the distance between the surface and particle at the mean penetration depth R in units of mean free path (at temperature T). Results for $T = 900$ K appear in Fig. 4. These results are in reasonable agreement with the experimental data. However our result [Eq. (45)] gives only a slight dependence of f on temperature, with f varying only $\sim 5\%$ through the range 300–900 K whereas Mills observes a marked temperature dependence with variation in f of as much as $\sim 100\%$ in this temperatuare range. This may indicate that the approximation of using Eq. (32) for $f(E,T)$ (i.e., calculating escape rate as though surface were completely absorbing) may not be valid at lower temperatures.[16] Other sources of discrepancy include the role of bulk and surface defects (mainly at temperatures greater than ~ 500) and trapping in the surface image potential well. In fact, very recent experiments[17] indicate that positron trapping–detrapping in the surface image well is involved in a good percentage of the emitted Ps fraction. A further deficiency is in the assumption that all positrons which leave the metal, leave as Ps. All these effects, however, will not qualitatively alter the general conclusion that the overall conversion efficiency is a substantial fraction for medium energies. Thus, the picture of a diffusive arrival of the positron at the surface from a characteristic stopping distance and subsequent capture of an electron with high probability after several attempts at tunneling through the surface appears to have some validity for medium-high incident energies and high temperatures.

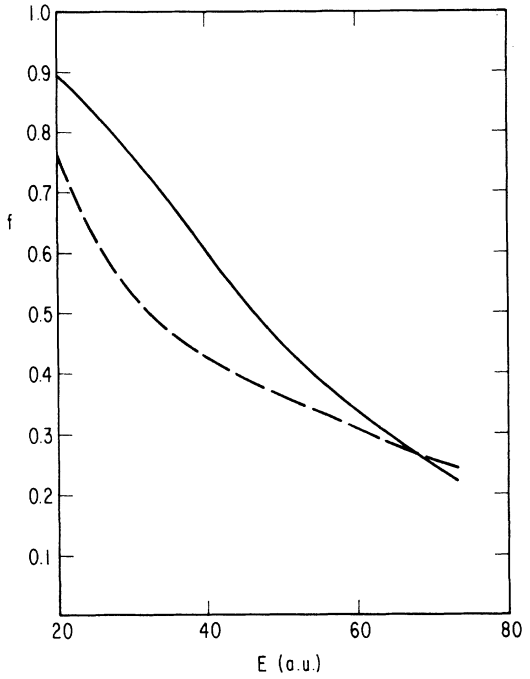

FIG. 4. Pickup fraction for Al vs incident positron energy ($T = 900$ K). Solid line: theory; dotted line: experiment (after Ref. 1).

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APPENDIX A: EQUIVALENCE OF A CORRELATED AND AN ISOTROPIC RANDOM WALK

We show that a correlated random walk on a three-dimensional cubic lattice such that at each step the particle is required to move in a direction 90° from the immediately preceding direction of movement is (provided the total number of steps is not too small) equivalent to an isotropic random walk on

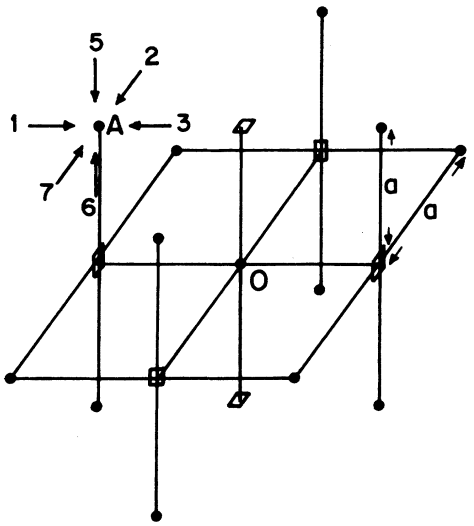

FIG. 5. Portion of three-dimensional cubic lattice. The dotted sites are accessible after two steps to a particle at O undergoing a correlated random walk where a 90° turn is required at each step.

the same lattice. We show a portion of the three-dimensional cubic lattice of lattice parameter a in Fig. 5. Clearly if the particle arrives at the site O at a given step, it must have been at one of the 12 dotted sites shown two steps previously. Looking at the site A, it is clear if the particle arrives at this site from the directions 1, 3, 5, or 6 that it has in each case one way of arriving at O two steps later, in each case with a probability of $(\frac{1}{4})^2$. But if the particle arrives at A from the direction 2 or 4 it has two ways of reaching O two steps later, again each way having a probability of $(\frac{1}{4})^2$. Thus, given a particle at A, the probability that the particle reaches O two steps later is given by (not knowing from which direction the particle at A arrived and assigning these directions equal probability) $\frac{1}{6}(1+1+1+1+2+2)\times 1/4^2=\frac{1}{12}$. Moreover the probability of reaching O in two steps from any of the 12 dotted sites is $\frac{1}{12}$. We may thus take the point of view that the particle is undergoing an "isotropic" random walk on a sublattice comprised of all points equivalent to the dotted points and not including points equivalent to the points with squares (i.e., an octahedral lattice of base $\sqrt{2}a$). Note that each "step" on the octahedral lattice corresponds to two steps on the cubic lattice. Now the probability $P_N(R)$ of a particle which is undergoing an isotropic random walk with step length l, to arrive at a positron R after N (N large) steps (and having started from the origin) is given by

$$P_N(R)=\left[\frac{3}{2\pi Nl^2}\right]^{3/2} e^{-3R^2/2Nl^2} \quad . \tag{A1}$$

It is obvious finally that $P_N(R)$ when evaluated for N with step length $\sqrt{2}a$ (for octahedral lattice walk) is the same as when evaluated for $2N$ with step length a (cubic lattice walk). Thus the above assertion on the correlated walk follows.

APPENDIX B: FRACTION OF PARTICLES UNDERGOING A THREE-DIMENSIONAL ISOTROPIC RANDOM WALK WHICH REACH AN ABSORBING SURFACE

We first evaluate the probability $Q_N(m)$ that a particle undergoing an isotropic random walk on an infinite three-dimensional (e.g., cubic, lattice parameter a) lattice arrives at a plane $x=ma$ for the first time after a total of N steps and after having started at the origin. We assume that all particles reaching this surface are removed from the system. Thus the total fraction of particles removed, $P(\mathfrak{N},m)$, after a total of $\mathfrak{N}$ collision times ($>m$) is given by

$$P(\mathfrak{N},m)=\sum_{N=m}^{\mathfrak{N}} Q_N(m) \quad . \tag{B1}$$

We first depict the projection of a typical random trajectory which passes unaffected through the surface $x=ma$ and ends at $x=(m-1)a$ after $N-1$ steps together with that of its "image" (see Fig. 6). The image trajectory is identical to the original trajectory up to the point of the first contact of the latter with the plane m. The remainder of the image trajectory is obtained by reflecting the remainder of the original trajectory through the plane m.[18]

It is clear that $Q_N(m)$ is given by the probability $P_N(m)$ of a particle arriving at the plane m after N steps in the absence of the requirement that it be removed upon contact with the plane m, minus the probability $P_N'(m',m)$ that after N steps the particle arrives at the plane $m'=m$ after having already made contact with the plane m at least once:

$$Q_N(m)=P_N(m)-P_N'(m,m) \quad . \tag{B2}$$

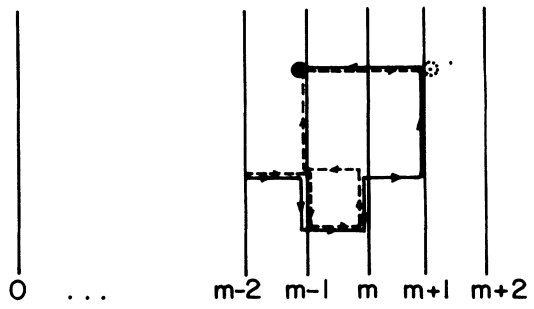

FIG. 6. Projection of a random trajectory and its "image" (dotted) near the plane m ignoring absorption. Given trajectory (image trajectory) ends at plane $m-1$ ($m+1$).

Now we see that

$$P'_N(m,m)=\tfrac{1}{6}[P'_{N-1}(m-1,m)+P'_{N-1}(m+1,m)+\tfrac{2}{3}P_{N-1}(m)] \quad . \tag{B3}$$

Equation (B3) states that $P'_N(m,m)$ is given by (the probability after $N-1$ steps that the particle is at $m-1$ after contacting m at least once) times (probability of reaching m at next step, i.e., $\frac{1}{6}$) plus (the probability after $N-1$ steps that the particle is at $m+1$ after contacting m at least once) times (probability of reaching m at next step, i.e., $\frac{1}{6}$) plus (the probability after $N-1$ steps that the particle is an m regardless of whether there was previous contact with m) times (probability of staying at m at next step, i.e., $\frac{2}{3}$). Clearly

$$P'_{N-1}(m+1,m)=P_{N-1}(m+1) \quad . \tag{B4}$$

In addition it is clear from the figure that every trajectory entering in $P'_{N-1}(m-1,m)$ is in one-to-one correspondence with and has the same probability as each trajectory (i.e., its image) entering in $P'_{N-1}(m+1,m)$. Thus,

$$P'_{N-1}(m-1,m)=P'_{N-1}(m+1,m)=P_{N-1}(m+1) \quad . \tag{B5}$$

Using Eqs. (B4), (B5), and (B3) we obtain

$$Q_N(m)=P_N(m)-\tfrac{1}{3}P_{N-1}(m+1)-\tfrac{2}{3}P_{N-1}(m) \quad . \tag{B6}$$

Now

$$P_N(m)=\int_{\text{slab }m}P_N(R)\,d^3R \quad , \tag{B7}$$

where $P_N(R)$ is given by Eq. (A1) (in the large-N limit) and where the integration is over the entire slab region of thickness a and bisected by the plane m. The integration is simple and we find

$$P_N(m)=\left[\frac{3}{2\pi N}\right]^{1/2}e^{-3m^2/2N}\,(1-e^{-3(N^2-m^2)N/2}) \quad . \tag{B8}$$

Finally using Eqs. (B8) and (B6) in Eq. (B1) we are led to the result Eq. (32) for $P(\mathfrak{N},m)$ [replacing summation by integration in Eq. (B1)]. It can be shown (though care must be taken in the subtraction of divergent quantities) that for $\mathfrak{N}\to\infty$

$$P(\mathfrak{N},m)\to 1 \tag{B9}$$

as expected.

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