energy, formula (8) will not be accurate under more general conditions.

With this reservation, it is interesting to compare measurements made by Rockwood[18] on variation of sputtering with current for argon-filled tubes. His points are fitted to Eq. (8) in Fig. 5. Treating the experimentally determined constants as before, and assuming that the ionic mean free path is just half the atomic mean free path because of electron exchange and that consequently the mobility of an argon ion in argon gas is half that of a potassium ion in argon we obtain $\epsilon_0=3.1$ ev and $dJ_0/dn=0.27$. These quantities agree as well as can be expected with their more accurate determination from the neon-argon discharge.

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[18] Private communication.

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On the Extraction of Electrons from a Metal Surface by Ions and Metastable Atoms*

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An elementary theory is developed for the process by which a helium ion or a 2^3S metastable helium atom may extract an electron from a metal surface. The helium ion after collision may become a neutral atom although sometimes an excited or even a metastable atom. In the case of the metastable atom the collision involves an exchange of electrons between the metal and the atom, the excess energy being carried away by the ejected L shell electron. The average distance of transition $\bar{s}$ for He^+ and for the 2^3S metastable helium atom is calculated for different velocities. For $v=10^5$ cm/sec., $\bar{s}_{\text{met}}=2a_0$ and $\bar{s}_{\text{ion}}=11.5a_0$ where $a_0=0.528\times10^{-8}$ cm. For $v=3\times10^7$ cm/sec., $\bar{s}_{\text{met}}$ comes out less than $0.1a_0$ and $\bar{s}_{\text{ion}}=6.0a_0$. These values are different from the values obtained by Massey in a similar computation. The theory accounts for some but not all of the experimental evidence. The probable shape of the potential that the metal surface offers to a metastable atom is found.

I. INTRODUCTION

A POSITIVE ion or a metastable atom colliding with a metal surface may undergo a collision of the second kind with the aid of one of the metallic electrons. In the case of a metastable atom whose radiative transition to the ground state is forbidden by the spin conservation selection rule $\Delta S=0$, the collision can involve an exchange of electrons between the metal and the atom which leaves the atom in a state of different multiplicity—let us say, the ground state. The positive ion simply captures the metallic electron, thereby becoming a neutral atom, although sometimes an excited or even a metastable atom. In the latter case, the metastable atom may decay with secondary electron emission.

The electron emission due to impact of mercury metastable atoms on a nickel surface was first definitely proved by Webb.[1] This was followed up by the work of Messenger[2] and Coulliette.[3] Sonkin[4] studied this electron emission using a tungsten surface under various conditions. Oliphant[5] also studied the emission of electrons from metal surfaces as a result of impact by helium metastable atoms. Besides the above-

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[1] H. W. Webb, Phys. Rev. **24**, 113 (1924).

[2] H. A. Messenger, Phys. Rev. **28**, 962 (1926).

[3] H. J. Coulliette, Phys. Rev. **32**, 636 (1928).

[4] S. Sonkin, Phys. Rev. **43**, 788 (1933).

[5] M. L. E. Oliphant, Proc. Roy. Soc. **A124**, 228 (1929).

mentioned direct studies, the extraction of electrons from metal surfaces by metastable atoms has been suggested as a mechanism to account for various phenomena. Uyterhoeven and Harrington[6] made use of the action of metastable atoms on metal surfaces to explain the emission of electrons from cold electrodes in discharges of neon, argon, and helium. In a similar manner Found and Langmuir[7] tried to explain the secondary emission from a negative probe in a neon discharge. Other authors[8–10] considered the action of metastable atoms on metal surfaces in their discussion of electrical and resonance radiation phenomena in gases, making use of some of the before-mentioned investigations. Penning[11] investigated the electron emission produced by positive neon ions which pass down a fine metal canal. Oliphant[5] pointed out that Penning's results probably include a contribution from metastable atoms produced as in his work.

The extraction of electrons by positive ion bombardment has been studied by many more people than the case of the metastable atoms. We shall mention only those where the energy of the bombarding ions is of the order of a few hundred volts. The reason for this limitation is that at higher energies the positive ion is able to eject secondaries from the metal by virtue of its motion besides merely capturing electrons due to its electric field. Oliphant[12] studied the electron emission from a metal surface due to He^+ bombardment. Chaudhri[13] investigated the secondary emission from a nickel surface by Hg^+ bombardment. He admitted the possibility that metastable mercury atoms could be responsible for part of the emission. Ramsauer and Kollath[14] studied the reflection of protons from solid bodies. Brasefield[15] measured the efficiency of argon ions and argon metastables in extracting electrons from a metal surface. Healea and Chaffee[16] studied the electron emission from a hot nickel target bombarded with molecular hydrogen ions. Veith[17] measured the ion reflection and the electron emission while bombarding metals with K^+. Guntherschulze and Bar[18] studied the emission of electrons from a MgO cathode in the glow discharge using He, Ne, A, H_2, N_2, and O_2. Healea and Houtermans[19] measured the electron emission and the ion reflection from a degassed nickel target bombarded by He, Ne, and A ions. Korff and Present[20] made use of the transition of ions into metastable atoms near a metal surface in their discussion of the discharge mechanism of Geiger counters. The energy involved in this process is thermal energy.

Oliphant and Moon[21] explained the neutralization of positive ions during a collision with a metal surface by the auto-electronic emission into a state of equal energy in the atom under the influence of the electrostatic field of the approaching ion. This theory was admittedly not made very precise. Massey[22] made a quantum mechanical calculation of the neutralization of a positive hydrogen ion when colliding with a metal surface and found the average distance at which this transition takes place. He assumed that for the case of a He^+ this distance is larger by a factor of two or more. He also made a similar calculation for the emission of electrons during the impact of metastable helium atoms and a metal surface. When the helium ion is neutralized, it may assume the triplet 2^3S state. He used perturbation theory to find the probability of a transition as a function of the distance from the metal surface and obtained the result that the probability of transition for the positive ions approached unity at a smaller distance from the

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[6] W. Uyterhoeven and M. C. Harrington, Phys. Rev. **35**, 438 (1930); **36**, 709 (1930).

[7] C. Found, Phys. Rev. **34**, 1625 (1929); I. Langmuir and C. Found, Phys. Rev. **36**, 604 (1930); C. Found and I. Langmuir, Phys. Rev. **39**, 237 (1930).

[8] K. K. Darrow, *Electrical Phenomena in Gases* (Williams and Wilkins, 1932).

[9] L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley & Sons, Inc., New York, 1939).

[10] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Company, New York, 1934).

[11] F. M. Penning, Vers. K. Ak. Amst. **36** (1927); Physics **8**, 13 (1928).

[12] M. L. E. Oliphant, Proc. Roy. Soc. **A127**, 373 (1930).

[13] R. M. Chaudhri, Proc. Camb. Phil. Soc. **28**, 349 (1932).

[14] C. Ramsauer and Kollath, Ann. d. Physik **16**, 560 (1933).

[15] C. J. Brasefield, Phys. Rev. **44**, 1002 (1933).

[16] M. Healea and E. L. Chaffee, Phys. Rev. **49**, 925 (1936).

[17] W. Veith, Ann. d. Physik **29**, 189 (1937).

[18] A. Guntherschulze and W. Bar, Zeits. f. Physik **107**, 11–12, 730 (1937); Zeits. f. Physik **108**, 11–12, 780 (1938).

[19] M. Healea and C. Houtermans, Phys. Rev. **58**, 608 (1940).

[20] S. A. Korff and R. D. Present, Phys. Rev. **65**, 253 (1944).

[21] M. L. E. Oliphant and P. B. Moon, Proc. Roy. Soc. **A127**, 388 (1930).

[22] H. S. W. Massey, Proc. Camb. Phil. Soc. **26**, 386 (1930); **27**, 460 (1931).

metal surface than for the case of the metastable atoms. This means that if helium ions and metastable 2^3S helium atoms are approaching a metal surface, the average distance at which the metastable atoms will decay is larger than the average distance at which the ions will be neutralized.

II. METASTABLE CASE

In this paper we shall show that in Massey's analysis of the metastable case the wrong matrix element was taken for the calculation of the decay constant. Taking the correct matrix element, one obtains the more reasonable result that the average distance for transition is larger in the case of the ion than in the case of the metastable atom. We proceed to develop our theory for the case of the triplet 2^3S metastable helium atom colliding with a metal surface.

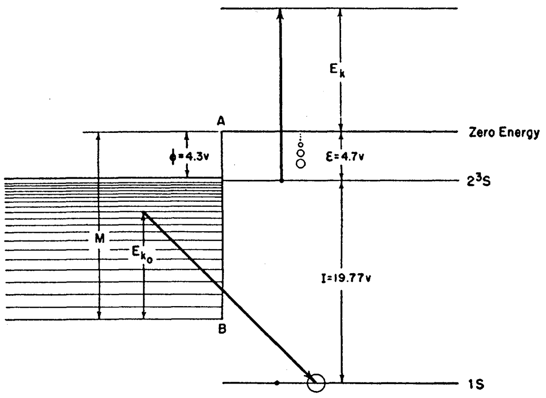

FIG. 1. Energy balance diagram for the extraction of electrons by metastable helium atoms from molybdenum. The region to the left of AB represents the potential well equivalent to the metal surface; the lines represent the continuous energy levels of the metallic electrons, the spacing of the lines roughly representing the density of the levels. The region to the right of AB represents the levels of the atomic electrons. The thick arrows indicate the transition which involves an exchange of electrons. An empty circle represents a vacancy in one of the atomic energy levels. A black dot represents an occupied level.

a. Energy Balance

Figure 1 shows the energy levels of the helium electrons, the metallic electrons, and the final free electron for the case of a Mo surface. The thick arrows indicate the transition which involves an exchange of electrons. The lines to the left of AB represent the continuous energy levels of the metallic electrons, the spacing of the lines roughly representing the density of levels. An empty circle represents a vacancy in one of the energy levels of the helium atom. A black dot represents an occupied level. Equating initial and final energies, we get for the transition shown

$$-M+E_{k0}-\epsilon=-(I+\epsilon)+E_k,$$

$$E_k=I-M+E_{k0},$$

where

I = energy difference between the 2^3S and the $1S$ states,
ϵ = energy of the 2^3S state,
E_{k0} = kinetic energy of the metallic electron,
E_k = energy of the free electron after the transition,
M = energy of the potential well which represents the metal.

From this equation and the values shown in Fig. 1 it is clear that any metallic electron is capable of making the transition in the case of a Mo surface.

b. Decay Rate

From the quantum mechanical theory of collision, one finds that the rate at which metastable atoms decay as a function of the distance s from the metal surface is

$$\lambda(s)=[nmk\Omega^2/\pi\hbar^3]|H|^2,$$

where

m = mass of the electron,
$\hbar=h/2\pi$ = Bohr unit of angular momentum,
$k=(2mE)^{\frac{1}{2}}/\hbar$, where E is the kinetic energy of the emitted electron,
n = density of free electrons,
Ω = volume used for normalizing the wave functions,

and H is the matrix element of the Hamiltonian for the transition where the initial state is a triplet 2^3S metastable helium atom and a free electron of momentum $\hbar k_0$ inside the metal and the final state is a helium atom in the ground state and a free electron of positive total energy and momentum $\hbar k$.

c. Matrix Element

The matrix element is the following:

$$H=\int\int\int \overset{*}{u}_{1s}(r_3)\overset{*}{u}_{1s}(r_2)[\exp(-i\mathbf{k}\cdot\mathbf{r}_1)]/\sqrt{\Omega}$$
$$\times\left[\frac{2e^2}{r_3}-\frac{e^2}{r_{13}}\right]u_{1s}(r_2)u_{2s}(r_1)$$
$$\times[\exp(i\mathbf{k}_0\cdot\mathbf{r}_3)]/\sqrt{\Omega}\,d\tau_1d\tau_2d\tau_3,\quad(1)$$

where the u's represent hydrogenic wave functions and the subscripts 1, 2, and 3 attached to the r's refer to the three electrons involved in the transition. e is the electronic charge.

$$u_{1s}(r_3)u_{1s}(r_2)=(1/\sqrt{\pi})(Z'/a_0)^{\frac{3}{2}}\exp(-Z'r_3/a_0)$$
$$\times(1/\sqrt{\pi})(Z'/a_0)^{\frac{3}{2}}\exp(-Z'r_2/a_0)$$
$$=[a^3\exp a(-r_2-r_3)]/\pi,$$
$$u_{1s}(r_2)u_{2s}(r_1)=(1/\sqrt{\pi})(Z_1/a_0)^{\frac{3}{2}}\exp(-Z_1r_2/a_0)$$
$$\times(1/4\sqrt{2\pi})(Z_2/a_0)^{\frac{3}{2}}(2-Z_2r_1/a_0)$$
$$\times\exp(-Z_2r_1/2a_0)=[(bc)^{\frac{3}{2}}/\pi]$$
$$\times(1-br_1)\exp(-br_1-cr_2),$$

where

$a_0=$ one Bohr radius $=0.528\times10^{-8}$ cm,

$a=Z'/a_0=1.69/a_0,$

$b=Z_2/a_0=1.19/a_0,$

$c=Z_1/a_0=2.04/a_0.$

The numerical values assigned to Z', Z_1, and Z_2 are those used by Bethe.[23]

This matrix element has the physical interpretation that in the initial state electron 3 is a metal electron, and electrons 1 and 2 are the atomic electrons; and that in the final state, electron 1 is a free electron, and electrons 2 and 3 are the atomic electrons.

Massey[22] starts with an expression which is identical to Eq. (1), but in his subsequent calculations he actually uses the following matrix element:

$$H=\int\int\int \overset{*}{u}_{1s}(r_1)\overset{*}{u}_{1s}(r_2)[\exp(-i\mathbf{k}\cdot\mathbf{r}_1)]/\sqrt{\Omega}$$
$$\times\left[\frac{2e^2}{r_3}-\frac{e^2}{r_{13}}\right]u_{1s}(r_2)u_{2s}(r_3)$$
$$\times[\exp i\mathbf{k}_0\cdot\mathbf{r}_3]/\sqrt{\Omega}d\tau_1d\tau_2d\tau_3.\quad(2)$$

This matrix element implies that electron 3 has initially both the wave function $\exp i\mathbf{k}_0\cdot\mathbf{r}_3/\sqrt{\Omega}$ and the wave function $u_{2s}(r_3)$ and that similarly electron 1 has finally the wave function $[\exp(-i\mathbf{k}\cdot\mathbf{r}_1)]/\sqrt{\Omega}$ and the wave function $u_{1s}(r_1)$.

The contribution from $2e^2/r_3$ in Eq. (1) is not very small because $u_{2s}(r_1)$ is not orthogonal to $[\exp(-i\mathbf{k}\cdot\mathbf{r}_1)]/(\Omega)^{\frac{1}{2}}$. If we were to use a more exact wave function for the free electron, the orthogonality would be better, and for this reason we neglect this contribution.

If we substitute for the u's the hydrogenic wave functions they represent, Eq. (1) becomes:

$$H=A\underset{\text{all space}}{\int\int\int}[\exp a(-r_2-r_3)-i\mathbf{k}\cdot\mathbf{r}_1]$$
$$\times[1/r_{13}](1-br_1)$$
$$\times\exp(-br_1-cr_2+i\mathbf{k}_0\cdot\mathbf{r}_3)d\tau_1d\tau_2d\tau_3.\quad(3)$$
$$A=[e^2a^3(bc)^{\frac{3}{2}}]/\pi^2\Omega.$$

Now we undertake the evaluation of H. The integration with respect to $d\tau_2$ can be carried out immediately. This gives a factor $8\pi/(a+c)^3$. The remaining integral

$$\underset{\text{all space}}{\int\int}[\exp(-ar_3-i\mathbf{k}\cdot\mathbf{r}_1)]$$
$$\times[1/|\mathbf{r}_1-\mathbf{r}_3|](1-br_1)$$
$$\times\exp(-br_1+i\mathbf{k}_0\cdot\mathbf{r}_3)d\tau_1d\tau_3\quad(3')$$

is rather complicated, but one can get a fairly good approximation, valid for large distances s of the atom from the metal surface; s being large compared to an atomic radius. Then $\exp(-ar_3)$ falls off much quicker than $1/|\mathbf{r}_1-\mathbf{r}_3|$, and one can substitute $1/|\mathbf{r}_1-\mathbf{s}|$ for the expression $1/|\mathbf{r}_1-\mathbf{r}_3|$.

The integral with respect to $d\tau_3$ is the following:

$$\int_0^{2\pi}\int_0^{\pi/2}\int_{s\sec\theta_3}^{\infty}[\exp ik_0r_3(\cos\theta_3\cos\theta_{k_0}$$
$$+\sin\theta_3\sin\theta_{k_0}\cos\phi_3)-ar_3]r_3{}^2dr_3\sin\theta_3d\theta_3d\phi_3,$$

where we have taken $\mathbf{s}$ as the polar axis and where the integration over θ_3 is taken from 0 to $\pi/2$ to take care of the fact that the wave function of the metallic electron is zero outside the metal. The integration with respect to ϕ_3 gives $2\pi J_0(k_0r_3\sin\theta_3\sin\theta_{k_0})$. Because of the overlapping of the wave functions, the integrand

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[23] H. Bethe, *Handbuch der Physik*, Vol. 24/1, p. 365.

will have non-vanishing values only for θ_3 small. Therefore we can replace the Bessel function by unity and do the rest of the integration immediately obtaining

$$2\pi[\exp(ik_0\cos\theta_{k0}-a)s]/as \times[-s^2/(ik_0\cos\theta_{k0}-a) + 2s/(ik_0\cos\theta_{k0}-a)^2-2/(ik_0\cos\theta_{k0}-a)^3].$$

The square of the absolute value of this expression is a factor in $|H|^2$, and we are interested in knowing how it depends on θ_{k0}. For $s=3a_0$ and $\theta_{k0}=\pi/2$ this absolute value squared is bigger by a factor of 1.44 than for the same s, but $\theta_{k0}=0$. For $s=4a_0$ the ratio is 1.40. If we assume k_0 to be zero, i.e., if we take the initial metallic electron to be at rest inside the metal, the integral becomes just

$$\int \exp(-ar_3)d\tau_3 = [2\pi/a_3](as+2)\exp(-as). \quad (4)$$

The square of this integral for $s=3a_0$ gives a value 1.32 times the value obtained when we assume k_0 to be perpendicular to the metal surface. Thus it is reasonable to believe that it does not matter very much whether the initial electron is at rest or moving in any direction whatsoever. The case of the electron moving perpendicularly to the metal surface but away from the surface gives a result identical to the case where the electron is moving towards the metal surface.

We now consider the integration with respect to $d\tau_1$. The integral we have to do is the following:

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}[1/|\mathbf{r}_1-\mathbf{s}|](1-br_1) \times[\exp(-br_1-i\mathbf{k}\cdot\mathbf{r}_1)]r_1^2dr_1\sin\theta_1\,d\theta_1\,d\phi_1.$$

We can expand $1/|\mathbf{r}_1-\mathbf{s}|$ in terms of spherical harmonics and $\exp(-i\mathbf{k}\cdot\mathbf{r}_1)$ in terms of spherical harmonics and Bessel functions. The integration over θ_1 and ϕ_1 can be done immediately.

The integration over r_1 reduces to

$$\int_0^{s}\sum_l(-i)^lP_l(\cos\theta_k)[r_1^{l+2}/s^{l+1}] \times\exp(-br_1)[1-br_1](\pi/2kr_1)^{\frac{1}{2}}J_{l+\frac{1}{2}}(kr_1)dr_1 + \int_s^{\infty}\sum_l(-i)^lP_l(\cos\theta_k)[s^l/r_1^{l-1}] \times\exp(-br_1)[1-br_1](\pi/2kr_1)^{\frac{1}{2}}J_{l+\frac{1}{2}}(kr_1)dr_1.$$

The integration with respect to dr_1 can be evaluated numerically for arbitrary values of s. For large s, one can obtain a good approximation by considering only the first integral and taking the limits of integration over r_1 from 0 to ∞ instead of from 0 to s.

We assume $\mathbf{k}$ to make an angle θ_k with the perpendicular to the metal surface and estimate its numerical value by letting $E_k=(19.77-4.3)$ ev, where 19.77 ev[24] is the difference in energy between the ground state and the 2^3S metastable state of helium, and 4.3 ev[25] is the approximate value of the work function of Mo, which is one of the metals Oliphant used. Neglecting all terms for which $l>2$, we get the following result:

$$(1.077\times10^{-24})/s-i(8.519\times10^{-23}\cos\theta_k)/s^2 + (6.520\times10^{-42}-1.955\times10^{-41}\cos^2\theta_k)/s^3.$$

Multiplying this expression by its conjugate, integrating over all space, and putting together our previous calculations, we find that the rate at which metastable helium atoms will decay is:

$$\lambda(s)=8nmk\Omega^2A^2\pi^2/\hbar^3a^4[8\pi/(a+c)^3]^2 \times\exp(-2as)[(3.956\times10^{-9}+0.796s)^2 + (3.268\times10^{-9}+0.404s)^2] \times[(2.320\times10^{-48})/s^2 + (5.033\times10^{-65})/s^4 + (7.649\times10^{-83})/s^6]. \quad (5)$$

This expression is a good approximation when s is of the order of $3a_0$ or greater.

One can find a reasonable value for $\lambda(0)$ by solving the problem anew for this special value of s. In this case one can no longer substitute $1/|\mathbf{r}_1-\mathbf{s}|$ for $1/|\mathbf{r}_1-\mathbf{r}_3|$ in the integral over $d\tau_1$ and $d\tau_3$. If we assume k_0 to be zero, the integral is as follows:

$$\int\int\exp(-ar_3-i\mathbf{k}\cdot\mathbf{r}_1)[1/|\mathbf{r}_1-\mathbf{r}_3|] \times(1-br_1)\exp(-br_1)f(r_3)d\tau_1d\tau_3,$$

where $f(r_3)$ is equal to unity inside the metal and is equal to zero outside the metal. We assume that half of the atom is inside the metal and the other half is outside, and take the polar axis per-

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[24] *Handbuch der Physik*, Vol. 24, p. 348.

[25] *Handbuch der Physik*, Vol. 14, p. 69.

pendicular to the surface. We expand $1/|\mathbf{r}_1-\mathbf{r}_3|$ in terms of spherical harmonics and $\exp(-i\mathbf{k}\cdot\mathbf{r}_1)$ in terms of spherical harmonics and Bessel functions. The limits of integration for θ_3 are from 0 to $\pi/2$; this takes care of the discontinuity of $f(r_3)$. The integration over θ_1, θ_3, ϕ_1, and ϕ_3 can be done immediately. Part of the integration over r_1 and r_3 was done analytically, and part was done numerically. When the values of the constants as already defined are used, the integral reduces to the following expression:

$$1.589\times10^{-41}+i[5.707\times10^{-42}P_1(\cos\theta_k)+9.077\times10^{-43}P_3(\cos\theta_k)]+\text{higher order terms.} \quad (6)$$

Squaring this expression, integrating over all space, and substituting in the expression for $\lambda(0)$, one finds $\lambda(0)=1.97\times10^{15}$ sec.$^{-1}$. We thus have found a value for $\lambda(0)$ and an analytic expression for $\lambda(s)$ which is a good approximation when s is of the order of $3a_0$ or greater. Figure 2 shows $\log_{10}\lambda(s)$ plotted against s. The heavy line was obtained from the expression for $\lambda(s)$ and therefore was extended into $s=3a_0$. Point A corresponds to $\log_{10}\lambda(0)$, and point C corresponds to $\log_{10}\lambda(3a_0)$; these two points are known fairly well. We have drawn a dotted line to show the probable value of $\log_{10}\lambda(s)$ for $s<3a_0$. For $s=2a_0$ we took k_0 perpendicular to the metal surface and performed the integration over $d\tau_3$ exactly and the integration over $d\tau_1$ numerically for this particular distance. In this integration we again substitute s for r_3 in the denominator of Eq. (3′), which is not too bad an approximation for $s=2a_0$. Using our results we can get a fairly good value for $\log_{10}\lambda(2a_0)$. Point B corresponds to this value and falls on the extrapolated curve as shown.

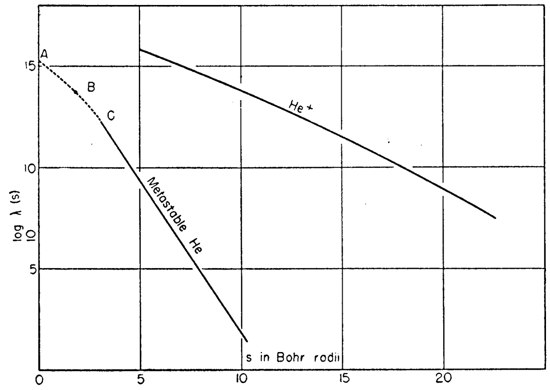

FIG. 2. Graph of $\log_{10}\lambda(s)$ as a function of s for He$^+$ and for 2^3S metastable He.

d. Probability of Transition

Actually the motion of the atom would make it necessary to derive a more complicated expression involving the time-variation of the perturbing potential. For velocities of collision such that the time-Fourier analysis of the perturbation does not contain appreciable amplitudes for frequencies of the order of an atomic frequency, one may regard the collision as adiabatic and use the time-independent perturbation at each distance. However, it is necessary to allow for the possible decay of the atom at some larger distance. Let $P(s)ds$ be the probability that the atom decays at position s in a distance ds. The probability that the atom reaches position s without decaying is

$$1-\int_s^\infty P(s)ds,$$

$$\therefore\quad P(s)=[\lambda(s)/v_0]\left[1-\int_s^\infty P(s)ds\right]ds,$$

where v_0 is the velocity of the helium atom, which we shall assume constant. The solution of this integral equation is

$$P(s)=B\exp\int\{1-d/ds[v_0/\lambda(s)]\}\lambda(s)/v_0 ds,$$

where B is a constant of integration.

Approximating $\lambda(s)$ by the simple exponential form $\lambda(s)=A\exp(-\alpha s)$, where $A=9.626\times10^{16}$ and $\alpha=7.303\times10^{8}$ we find the expression for $P(s)$ becomes

$$P(s)=F\exp[-(A/v_0\alpha)\exp(-\alpha s)-\alpha s],$$

where F is a constant.

From the integral equation it is easy to see that for large s

$$P(s)=\lambda(s)/v_0=[A/v_0]\exp(-\alpha s)$$

and from the solution for $P(s)$ it is obvious that for large s

$$P(s)=F\exp(-\alpha s),$$

$$\therefore\quad F=A/v_0$$

and

$$P(s)=[A/v_0]\exp[-(A/v_0)\exp(-\alpha s)-\alpha s].$$

Figure 3 shows a graph of $P(s)$ against s for $v_0=10^5$ cm/sec. It should be noted that the exponential form taken for $\lambda(s)$ keeps on increasing for values of $s<2a_0$ while the graph of $\log_{10}\lambda(s)$ indicates that $\lambda(s)$ probably levels off. For this reason the graph of $P(s)$ may probably be less steep on the side of small s than is shown on Fig. 3. To get $\bar{s}$ the average distance for transition, one has to do the integral

$$\int_0^\infty sP(s)ds,$$

which can be done graphically or analytically. For $v_0=10^5$ cm/sec., $\bar{s}=2a_0$ which is very near s_m, the value of s for which $P(s)$ is a maximum. For $v_0=3\times10^7$ cm/sec. s comes out less than $0.1a_0$. This last value of $\bar{s}$ does not have very much meaning because of the breakdown of the perturbation theory and the crudeness of the model used for the metal. For this velocity Massey[22] obtained a value of $\bar{s}$ of the order of $3a_0$, which according to our calculations is certainly too high. A very good approximation to $\bar{s}$ can be obtained by finding the s for which

$$\int_s^\infty \lambda(s)/v_0 ds=1.$$

For $v_0=10^5$ cm/sec. one gets $1.9a_0$ for $\bar{s}$.

TABLE I. Relation between the velocity component perpendicular to the metal surface and the percentage of metastable atoms reflected.

Vel. perpendicular to surface in 10^6 cm/sec.	Percentage of ref. met. (Oliphant's results)	Average percentage
2.6	60 to 90	75
4.5	40 to 60	50
7.0	40 to 70	55
7.8	>50	
9.9	40	40
12.0	15 to 40	28
14.0	40 to 50	45
17.0	10 to 30	20
20.0	10 to 20	15
32.0	5	

From Oliphant's[12] results (shown in Table I) of the percentage of reflected metastable atoms at different velocities and different angles of incidence, it can be seen that the percentage of reflected metastable atoms varies fairly linearly with the component of velocity perpendicular to the surface. This might indicate that the percentage of reflected metastable atoms depends mainly on how close the atoms get to the metal surface.

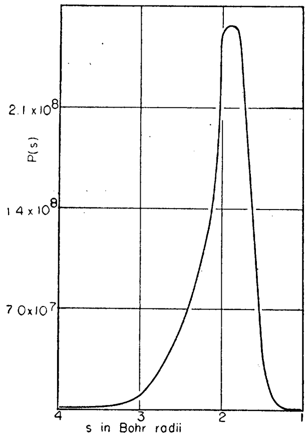

FIG. 3. Graph of $P(s)$ as a function of s for metastable helium atoms of velocity 10^5 cm/sec.

From these data one could calculate the distance from the metal surface at which most atoms turn back. Let us call this distance s_R. An approximate value of s_R can be obtained by solving for s_R in the equation

$$R=1-2\int_{s_R}^\infty \lambda(s)/v_0 ds,$$

where R is the fraction of reflected metastable atoms. Knowing the initial energy of the metastable atoms and knowing where they turn back, one can get the shape of the repulsive potential that the surface offers to the metastable atoms. Figure 4 shows this potential as a function of s. In this analysis we have neglected the fact that we should use $P(s)$ instead of $\lambda(s)$ and v instead of v_0, where v is the instantaneous velocity. When we found $P(s)$ previously, we assumed that the atom decayed on its ingoing trip, but if we now consider the reflection coefficient R, we must solve the problem more rigorously. Let us call $P_i(s)$ the $P(s)$ we already calculated, meaning that it is the probability that the atom decays on its ingoing trip. To get an expression for $P_0(s)$, the probability that the atom decays on its outgoing trip, one must solve the integral equation

$$P_0(s)=\left[1-\int_{s_R}^{\infty}P_i(s)ds-\int_{s_R}^{s}P_0(s)ds\right]\lambda(s)/v_0.$$

The solution of this equation is

$$P_0(s)=[A/v_0]\exp\left[-\alpha s+(A/\alpha v_0)\times\exp(-\alpha s)-(2A/\alpha v_0)\exp(-\alpha s_R)\right].$$

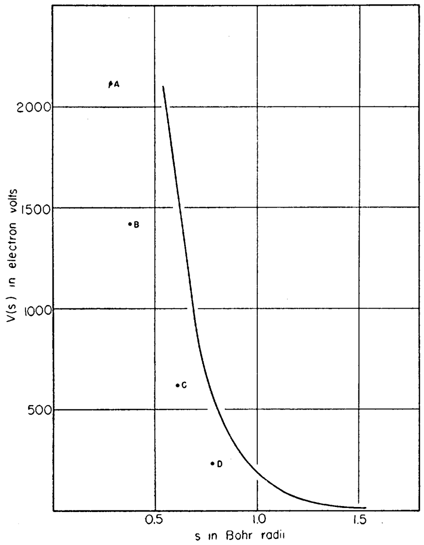

FIG. 4. Potential offered by a metal surface to a 2^3S helium atom.

Now s_R can be obtained by solving the equation

$$R=1-\int_{s_R}^{\infty}P_i(s)ds-\int_{s_R}^{\infty}P_0(s)ds=\exp\left[-(2A/\alpha v_0)\exp(-\alpha s_R)\right].$$

Calculating s_R from this formula, one finds that the curve representing the potential that the surface offers to the metastable atom is closer to the surface than what was previously obtained as shown by points A, B, C, and D on Fig. 4. We now correct for the fact that the velocity of the metastable atoms is not a constant v_0 but a function $v(s)$ which can be obtained from v_0 and the potential curve already found. By a process of iteration, the potential curve can be improved. Plotting $v(s)$ against s, one can find an analytic expression that fits the curve obtained. One can now find $P_i(s)$ and $P_0(s)$ by again solving the integral equations

$$\left[1-\int_{s}^{\infty}P_i(s)ds\right]\lambda(s)/v(s)=P_i(s),$$

$$\left[1-\int_{s_R}^{\infty}P_i(s)ds-\int_{s_R}^{s}P_0(s)ds\right]\lambda(s)/v(s)=P_0(s).$$

Again s_R was obtained from the equation

$$R=1-\int_{s_R}^{\infty}P_i(s)ds-\int_{s_R}^{\infty}P_0(s)ds.$$

This second correction brought the potential curve almost to coincide with the curve obtained by using

$$R=1-2\int_{s_R}^{\infty}\lambda(s)/v_0ds.$$

This means that apparently the two errors involved in using this approximation cancel each other. It is unfortunate that both Oliphant's results and our theory are rather crude and that therefore the curve we obtained is only a rough approximation. It does, however, indicate a method to obtain information about the repulsion of atoms by metals. The theory can probably be improved considerably when there is need for it, so that more precise data on the reflection of metastables from metal surfaces are to be desired highly.

e. Angular Dependence

Equations (5) and (6) show that if the transition takes place at the metal surface or at large distances from the surface, there is practically no angular dependence. No detailed experiments have been carried out to test this angular dependence, but Oliphant informed Massey[22] that he found no electrons ejected at an angle less than 15° with the surface. Our theory does not predict such angular distribution, and for this feature a more refined theory or experimental procedure is needed. For the special value $s=2a_0$ the integral over $d\tau$ gives

$$4\pi\times10^{-18}\{5.246P_0(\cos\theta_k)+2.916P_2(\cos\theta_k)-0.407P_4(\cos\theta_k)+0.017P_6(\cos\theta_k)+i[2.370P_1(\cos\theta_k)-1.350P_3(\cos\theta_k)+0.093P_5(\cos\theta_k)-0.003P_7(\cos\theta_k)]\}+\text{higher order terms.}$$

An expression whose absolute value squared has an angular dependence is shown in Fig. 5.[26] For thermal velocities this is the average distance of transition, and hence from our theory we should expect some angular dependence for these velocities. Oliphant's velocities were of the order of 10^7 cm/sec., and thus the atoms penetrated closer than $2a_0$ before decaying, making the angular distribution even less than that shown in Fig. 5.

Massey[22] explains the angular distribution found by Oliphant by assuming that "the portion of the wave function which gives rise to the ejection of electrons is that which falls within the boundary of the metal." Hence when a transition occurs, he regards the atomic electron as overlapping the metal, and when this electron is replaced by the metallic electron, it must therefore pass through the metal surface. Massey further states that the electron will be refracted similarly to a ray of light going from one medium to an optically denser one. There seems to be no basis for the assumption that the atomic electron must always be inside the metal for the transition to take place, as an inspection of Eq. (1) clearly shows. Again, we would expect that when the electron is refracted as it passes out through the metal surface, it is refracted away from the normal because its initial velocity parallel to the surface is unaltered after going through the surface but its normal velocity is diminished because of the work function. Hence if we were to include this effect in our theory, it would decrease the preference for electron emission perpendicular to the metal surface.

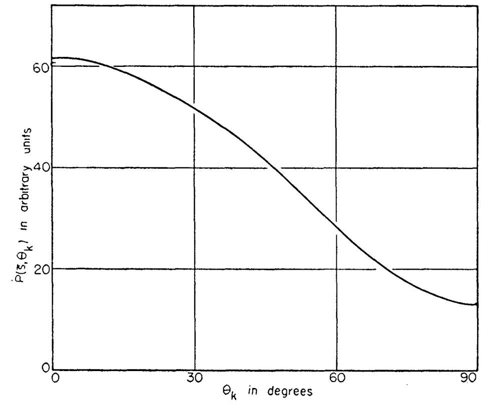

FIG. 5. Graph of $P(\bar{s}, \theta_k)$ as a function of θ_k for 2^3S helium atoms of velocity 10^6 cm/sec.

III. HELIUM ION CASE

a. Energy Balance

The case of the helium ion colliding with a metal surface can be solved in a way analogous to the case of the helium metastable atom. Figure 6 shows the energy balance diagram for a Mo surface. This diagram shows that inside the metal there are electrons whose energy level is identical or very nearly identical to the 2^3S orbit. When the ion gets near the metal surface the potential field to which the metallic electrons are exposed is altered, and one of the above-mentioned electrons may pass through the metal surface and occupy the 2^3S orbit. In the case of Mo there are no electrons whose energy level is identical to the 2^1S or $1S$, and for this reason the only probable transition is the one to the 2^3S state. In the case of Pt, the work function is 5.01, 5.1, or 6.0 v[27] as obtained by different investigators, and our diagram would show that then the transition to the 2^3S would be impossible. This is not exactly correct because as the temperature of the surface increases, some of the higher electronic cells will be occupied. As shown by Sonkin[4] the behavior of a metallic surface is very easily affected by the conditions of the surface.

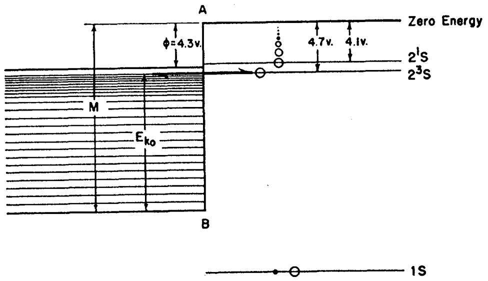

FIG. 6. Energy balance diagram for the extraction of electrons by helium ions from molybdenum. This diagram should be interpreted as explained under Fig. 1.

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[26] For this computation and for most of the other computations the WPA tables of exponential function and the WPA table of spherical Bessel functions were used.

[27] *Handbuch der Physik*, Vol. 14, p. 69.

b. Matrix Element

In this case the matrix element is

$$H=\int\int\int[\overset{*}{u}_{2s}(r_1)\overset{*}{u}_{1s}(r_2)-\overset{*}{u}_{2s}(r_2)\overset{*}{u}_{1s}(r_1)]$$
$$\times[-Ze^2/r_2+e^2/r_{12}]u_{1s}(r_1)$$
$$\times[\exp i\mathbf{k}_0\cdot\mathbf{r}_2]/\sqrt{\Omega}d\tau_1 d\tau_2$$

where the variable r_2 must remain inside the metal. A good approximation for H can be obtained for large s by replacing r_{12} by r_2. If we make this assumption, H reduces to

$$H=\int\int(1-br_2)\exp(-br_2-cr_1)[1/r_2]$$
$$\times\exp[-ar_1+ik_0(\cos\theta_{k0}\cos\theta_2$$
$$+\sin\theta_{k0}\sin\theta_2\cos\phi_2)]d\tau_1 d\tau_2.$$

The integration over $d\tau_1$ can be done immediately. The integration over $d\tau_2$ can be done without much difficulty if we expand the Bessel function obtained from the integration over ϕ_2 and take only the first term of the expansion. The final result is

$$H=16\pi^2/(a+c)^3[\exp(ik_0\cos\theta_{k0}s-bs)]/bs$$
$$\times[(bs^2-s)/ik_0\cos\theta_{k0}-b$$
$$+(1-2bs)/(ik_0\cos\theta_{k0}-b)^2$$
$$+2b/(ik_0\cos\theta_{k0}-b)^3].$$

The value of $|H|^2$ can be found for any large distance s and any direction of $\mathbf{k}_0$. For s of the order of $10a_0$ we found that the value when $\mathbf{k}_0$ was parallel to the metal surface was about four times the value when $\mathbf{k}_0$ was perpendicular to the metal surface. We took an average of these two values.

c. Decay Rate

The rate at which ions decay as a function of the distance from the metal is now given by $\lambda(s)=[mk_0\Omega/\pi\hbar^3]|H|^2$. This expression unlike the corresponding one for the case of the metastable atom does not have a factor $n\Omega$, the number of free electrons. This extra factor arose because in the averaging over k_0 all free metallic electrons were available. Any excess energy could be carried away as kinetic energy by the ejected L shell electron. In the case of the ion there is no final outgoing electron, so the energy of the metallic electron capable of performing the transition is uniquely defined by energy conservation within the limits of the uncertainty principle. When the numerical values of the constants are substituted,

$$\lambda(s)=2.390\times10^{49}\exp(-2.254\times10^8 s)$$
$$\times[s/b+1/b^2+1/b^3 s]^2.$$

Figure 2 shows a graph of $\log_{10}\lambda(s)$ as a function of s.

One can find $\bar{s}$ the average distance of transition from the integral

$$\bar{s}=\int_s^\infty sP(s)ds.$$

As previously shown, a good approximation is obtained by finding the s at which

$$\int_s^\infty \lambda(s)/v_0 ds=1.$$

For $v_0=10^5$ cm/sec., $\bar{s}=11.5a_0$ and, for $v_0=3\times10^7$ cm/sec., $\bar{s}=6.0a_0$.

Massey solved the case of a hydrogen ion which collides with a metal surface and performs the transition to the 2^3S state. He found that for $v_0=3\times10^7$ cm/sec. $\bar{s}_{\mathrm{H}^+}$ is of the order of $1a_0$, and then assumed that $\bar{s}_{\mathrm{He}^+}$ might be bigger by a factor of two or more. We calculated $\bar{s}_{\mathrm{H}^+}$ for $v_0=3\times10^7$ cm/sec. and obtained an $\bar{s}$ of the order of $5a_0$. For the case of the hydrogen ion Massey used the correct matrix element but did not evaluate the integrals correctly.

IV. DISCUSSION

The extraction of electrons by He$^+$ colliding with a metal surface may be explained as the result of two separate processes. First the ion is neutralized, becoming a 2^3S metastable atom, and then if the metastable atom can get closer to the metal surface than $\bar{s}_{\mathrm{met}}$, it will have a very high probability of assuming the ground state, the resulting energy being used in extracting an electron from the metal. Figure 7 shows that our values $\bar{s}_{\mathrm{He}^+}$ and $\bar{s}_{\mathrm{met}}$ for thermal velocities permit such a double process. For $v_0=3\times10^7$ cm/sec. $\bar{s}_{\mathrm{met}}$ might seem too small to permit ions to be reflected as neutrals, but one must remember that

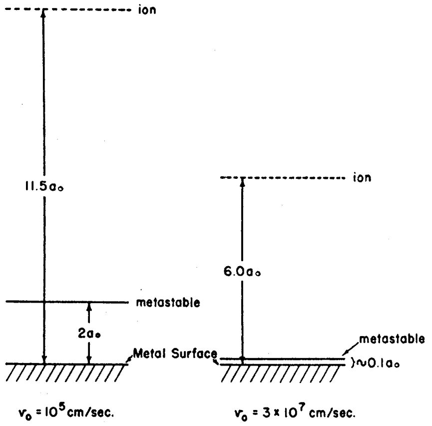

FIG. 7. $\bar{s}$ for 2^3S helium atoms and for He^+ for two different velocities.

this is an average distance, which means that some ions after being changed into metastables will decay at a distance greater than $0.1a_0$. Besides, at these very small distances our theory can give only very approximate results.

Oliphant and Moon[21] in their discussion of the helium ion proposed the theory that the inverse transition metastable→ion was highly improbable because once the transition ion→metastable takes place the remaining metallic electrons would fill the cell previously occupied by the electron which is extracted from the metal. This would be true if the relaxation time were of the order of 10^{-15} sec. or less. A rigorous calculation of the relaxation time[28] is too involved, and we shall not attempt it. Nevertheless, our value of $\bar{s}_{\mathrm{He}^+}$ ($6.0a_0$ for $v_0 = 3\times10^7$ cm/sec.) indicates that a beam of He^+ ions colliding with a metal surface will be almost completely transformed into metastable and neutral atoms unless the metastable→ion transition is also highly probable. When Oliphant[12] produced a beam of metastable atoms by sending a beam of helium ions at a small angle with the metal surface, he also obtained many reflected ions which he removed from the beam by means of an electric field. This experimental evidence indicates that the relaxation time is too long to prevent the metastable →ion transition to take place.

We will therefore assume that the metallic electron will oscillate between the metal and the ion (Schüttelwirkung) once the ion gets closer to the metal surface than $\bar{s}_{\mathrm{He}^+}$. Thus if a beam of ions is sent against a metal surface, once they are closer to the metal surface than the $\bar{s}_{\mathrm{He}^+}$, they can no longer be identified as ions or metastable atoms.[29] The probability that an ion finally may achieve the ground state depends on how close the particle can get to the metal surface and on the number of ion⇄metastable jumps that can occur. These two factors depend on the energy of the ion, but the problem of finding this functional dependence is too involved.

ACKNOWLEDGMENT

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[28] From dimensional considerations one may guess the following expression for τ.

$$\tau = A/[vn^{\frac{1}{3}}(e^2n^{\frac{1}{3}}/mv^2)^2],$$

where v is the velocity of the metallic electrons, n their density, m the electronic mass, and e the electronic charge. A is an undetermined constant. The numerical computation shows that $\tau \sim A\,10^{-14}$ sec.

[29] Most metals have a work function less than 5.0 volts and for this reason if 2^3S helium atoms are sent against these metals at absolute zero, all the electronic cells are filled up and the metastable atoms would remain as metastables until they perform the transition to the ground state and extract an electron.