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Neutralization of Ions and Ionization of Atoms Near Metal Surfaces*

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Conditions are examined for the resonance transfer of an electron between a metal and an ion or an atom in close proximity to the surface. The point of view is that of Franck-Condon crossings of potential energy curves of the initial and final states of the system. The effect of ion image forces is found in many cases to cause a significant variation of transition probability with distance. As a result, the conditions for neutralization of a rare gas ion to a metastable state and its subsequent de-excitation with the ejection of a secondary electron is found to be severely restricted. In particular, the theory of Cobas and Lamb for the ejection of electrons by the incidence of He$^+$ on a Mo surface are found to be seriously in error. In such cases an Auger type de-excitation is believed to be the mechanism for secondary electron emission.

I. INTRODUCTION

When an ion or an atom approaches a metal surface, neutralization or ionization processes are often possible. An electron may tunnel through the potential barrier between the metal and a positive ion to effect a neutralization. In a similar manner an atom may be ionized if an atomic electron tunnels to any unoccupied electronic state in the metal. The ion neutralization process is of particular interest because of the role it may play in the process of secondary electron emission from a metal surface bombarded by positive ions. For the case in which a monatomic helium ion is the bombarding particle, it has been proposed[1,2] that the ion becomes neutralized to the $^3S_1$ metastable state a short distance from the metal. On closer approach it is thought that the metastable de-excites by an exchange of electrons, i.e., the outer atomic electron is ejected simultaneously with the capture of a metal electron into the ground atomic state. The ejected electron appears as an ion-induced secondary electron.

Oliphant and Moon[3] were the first to suggest that a metal electron might tunnel through a potential barrier to neutralize an approaching positive ion. Quantitative quantum-mechanical calculations of the transition probability were made by Shekhter[4] for the transition of a hydrogen atomic ion near a molybdenum surface to the lowest excited state of the atom. Shekhter modified the results to represent the approach of He$^+$. Similar calculations for the transition of He$^+$ to the He($^3S_1$) metastable state near a molybdenum surface were made by Cobas and Lamb[2] who used hydrogenic wave functions for the helium atom and ion.

These explanations were based on the model shown in Fig 1. The metal is represented by a potential box of depth W_a, filled with N electrons to the Fermi level ζ. The work function ϕ is the minimum energy required to raise an electron to the energy continuum. At normal temperatures so few electronic states are occupied above the Fermi level that they are neglected in this explanation. The ion is represented by a potential well which may be occupied by an electron at definite levels to form an atom. The atom of ionization potential V_i is shown in an excited state of excitation potential V_e. In order for the neutralization to take place, the energy level of the electron in the metal must coincide within narrow limits with that in the atom. The two states are then said to be in resonance and a tunneling transition may take place. Thus, the transition may occur if

$$W_a > V_i - V_e > \phi. \tag{1}$$

For the reverse process, ionization of an atom by a metal, it is necessary that the electron from the atom undergo a transition to an unoccupied electronic state in the metal. This requires that

$$\phi > V_i - V_e. \tag{2}$$

The same method of reasoning is applicable to other resonance processes. An atom may capture a metal electron to form a negative ion or a negative ion may be stripped of an electron. Conditions analogous to Eqs. (1) and (2) result.

These results have been based upon a model of two independent potential systems. However, not only is the potential barrier between the ion and the metal lowered at close approach, but the entire shape of the ionic potential well is deformed. This deformation necessarily alters the energy levels of an electron in the

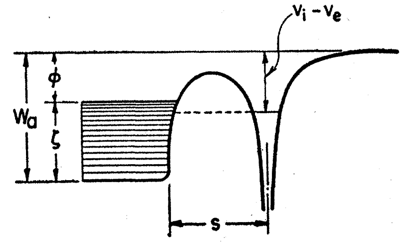

FIG. 1. Representation of energy levels of an electron in the field of a metal and an ion separated by distance s.

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* It has come to the author's attention during the preparation of the manuscript that H. D. Hagstrum has arrived independently at some of the conclusions obtained in this paper.

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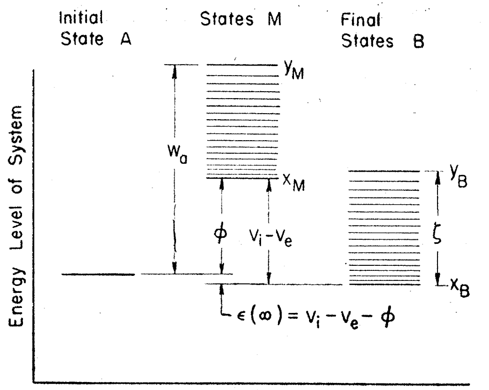

FIG. 2. Energy levels of system for neutralization of an ion at infinite separation. Initial state A: N electrons in metal plus an ion at infinity. States M: N-1 electrons in metal plus an ion and an electron at infinity. Final states B: N-1 electrons in metal plus an excited atom at infinity.

well. These effects can be taken into account by a quantum-mechanical determination of the perturbed energy levels of an electron in the deformed well. In this paper, however, a different approach to the problem will be employed. The electronic state of the total system, including both the atomic and metal systems, is specified both before and after transition. In computing the electronic energy of these total system states, use is made of the identity of this electronic energy with the nuclear potential energy. With regard to the likelihood of electronic transitions between the initial total state and the final total state, use is made of the Franck-Condon principle. The Franck-Condon principle states that an electronic transition can occur with appreciable probability only when the position and velocity of the approaching particle is unaltered by the transition. Conservation of energy then requires that the nuclear potential energy (electronic energy) be unchanged as a result of transition.

It is possible to analyze a number of neutralization and ionization processes involving both positive and negative ions at metal surfaces. Because of their particular relevance to secondary electron emission, detailed analyses will be made of the neutralization of a positive ion and the ionization of an atom.

II. NEUTRALIZATION OF A POSITIVE ION

A description of the initial state of the system includes both the metal and the approaching ion. A final state of the system includes the metal less one electron and the neutralized atom. The potential energy level associated with each of these states of the system is considered to be a function of the separation s between the metal surface and the approaching particle. When the potential energy curve for the initial state of the system crosses that for a possible final state of the system, a transition may take place according to the Franck-Condon principle. The states of the system are described as follows:

Initial state A: N electrons in the metal plus an ion at separation s.

Final states B: N-1 electrons in the metal plus an atom at separation s.

They can be referenced relative to one another by a consideration of the levels for infinite separation and zero kinetic energy. In Fig. 2 the energy level of initial state A at infinity is chosen arbitrarily. It is convenient to employ a set of states M describing N-1 electrons in the metal plus an ion and electron at infinity. Each one of the states M is constructed by removing to infinity one of the electrons in the metal. If an electron at the Fermi level is removed to infinity, the potential energy of the system is raised an amount ϕ. This is shown as level x_M in the diagram. Correspondingly, if the electron removed to infinity is taken from the bottom of the band of metallic states, the level is raised by an amount W_a to give state y_M. There exist N possible choices of electrons to be removed giving rise to a band of N states between x_M and y_M possessing an inverted Fermi distribution.

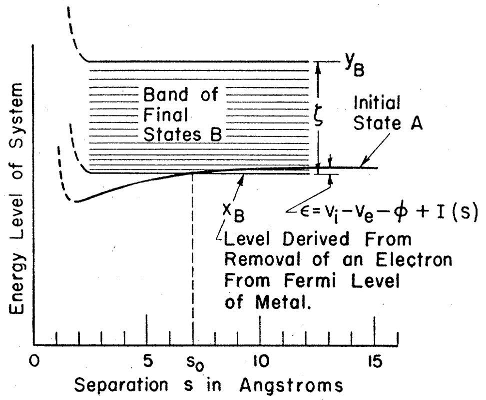

FIG. 3. Energy levels of system as a function of separation for neutralization of the He$^+$ ion to the He($^3S_1$) metastable state at a molybdenum surface. Initial state A: N electrons in metal plus an ion at distance s. Final states B: N-1 electrons in metal plus an excited atom at distance s.

The final set of states B at infinity is constructed by allowing the ion and electron of one of the states M to recombine at infinity forming an excited atomic state of energy V_e (V_e is zero for the ground state). This lowers the energy of a state M by an amount $V_i - V_e$. Each state M gives rise to a possible final state B, resulting in a simple displacement of the band of states M. The set of states M need be considered no longer.

The energy changes in the system associated with the approach of the atom or ion to the surface are shown in Fig. 3. The distance scale is appropriate to the neutralization of the monatomic He$^+$ ion to the He($^3S_1$) metastable state on a Mo surface. Because the final states B involve a neutral atom, the energy levels are expected not to vary with distance at distances greater than an atomic "radius" if the small van der

Waals contribution is neglected. At closer distances, the repulsion between the atom and the surface causes the potential curves to rise sharply in a manner similar to those describing the collision of two atoms. Because the detailed nature of the repulsive part of the curve is unknown, only the qualitative behavior is indicated by dashed lines. The image force to which the ion is subjected lowers the level of the initial state A below the infinite separation level by the image potential,

$$I(s) = -e^2/4s.$$

As with levels B, the repulsion between the ionic core and the metal is indicated qualitatively by dashed lines.

It should be emphasized that the levels of Fig. 3 are levels associated with the total system. Although the final states were derived from the free-electron states of the metal, they are to be regarded not as states of the metal, but as states of the entire system available for occupancy in a transition.

It is clear from Fig. 3 that Franck-Condon crossings of initial state A with possible final states B occur only at distances greater than s_0 for the example chosen (He$^+$ on Mo). Since the ionic "radius" is smaller than that of the atom, the distance at which level A rises sharply is expected to be smaller than the distance at which levels B rise sharply. Hence, on this simple picture, a recrossing of potential curves is not expected for the case shown.

In order to obtain a condition similar to Eq. (1), but modified to take account of variation in energy levels, it is useful to define ϵ, the difference in energy between initial state A and final state x_B of the system. It is shown in Fig. 3. State x_B corresponds to the removal of an electron from the Fermi level of the metal. The value of ϵ appropriate to infinite separation can be obtained by inspection from Fig. 2. The variation of ϵ with distance is given by

$$\epsilon = V_i - V_e - \phi + I(s),$$

when repulsion effects are neglected. The neutralization transition can take place if the curve representing the initial state crosses a curve for a possible final state. Such crossings exist if

$$\zeta > \epsilon > 0.$$

This equation may be expressed in the form

$$W_a > V_i - V_e + I(s) > \phi, \tag{3}$$

for comparison with Eq. (1). It is clear that previous treatments have ignored the effect of the image potential.

The results above apply rigorously only at absolute zero. At a finite temperature a few electrons are excited above the Fermi level giving rise to a few final states B below level x_B. Although the second inequality of Eq. (3) implies the absence of such states, no significant violation of the condition is expected.

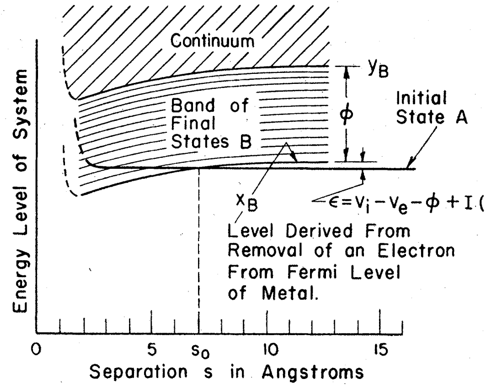

FIG. 4. Energy levels of system as a function of separation for ionization of the He($^3S_1$) metastable atom at a molybdenum surface. Initial state A : N-1 electrons in metal plus an excited atom at distance s. Final states B : N electrons in metal plus an ion at distance s.

III. IONIZATION OF AN ATOM

Ionization of an atom near a metal surface is essentially the reverse of the process considered in the last section. The intitial and final states are described similarly but the roles are reversed (compare Figs. 3 and 4). As before, these states are referenced at infinity. A state M (as in Fig. 2) consisting of N-1 electrons in the metal plus an electron and an ion at infinity is formed by ionizing the atom of initial state A at infinity. This raises the level of the system by an amount $V_i - V_e$. The electron at infinity is then allowed to occupy one of the unfilled levels above the Fermi level in the metal potential well. If the electron occupies the Fermi level, the final state of the system is lowered below level M by the work function of the metal ϕ. All states above the Fermi level to the top of the potential well are available giving rise to a band of final states of width ϕ. There exists a continuum of final states above level y_B, corresponding to states in which an electron is not bound to the metal.

The dependence of the energy levels as a function of s is shown in Fig. 4. The distance scale is appropriate to the ionization of the He($^3S_1$) metastable atom on a Mo surface. Since the initial state involves an uncharged particle, the level is unmodified for the larger values of s. The set of final states is modified by the image potential. The effect of close-in repulsive forces is indicated by the broken curves.

A transition can occur when the curve for initial state A crosses the band of final states B. A condition similar to that found in Sec. III results,

$$\phi > V_i - V_e + I(s). \tag{4}$$

This expression replaces Eq. (2). It can be seen that the inequality is the same as before but modified by the image potential. As before these results apply only at absolute zero. At finite temperatures a few states will exist below level x_B in Fig. 4, but are not expected to cause a significant violation of Eq. (4).

The inclusion of image potential in the present theory leads to a number of cases of interest depending on the values of V_i, V_e, and ϕ.

(a) As illustrated in Fig. 4, when $V_i - V_e$ exceeds ϕ by a small amount, ionization can occur for distances such that $s < s_0$, a possibility previously excluded.

(b) For a highly excited atom, $V_i - V_e$ is very small. The initial state A of Fig. 4 is raised so that at large s it lies just below level y_B. It can be seen that curve A will then cross the continuum of final states at small s. Thus the excited atom may be ionized at close approach, with the possibility of the electron appearing as a secondary electron.

(c) In certain cases when very slow atoms are ionized they possess insufficient kinetic energy to overcome the image potential and become trapped. This is particularly true for the vapors of the alkali metals. The ionization potentials are sufficiently low that ionization can occur near most metal surfaces. The trapped ions will eventually reach thermal equilibrium with the surface and form an adsorbed layer.

(d) An ion that has become neutralized at distances greater than s_0 may be ionized again at closer approach and be reflected as an ion. Such an ion loses kinetic energy equal to the difference in potential energy at the neutralization and ionization distances. Even if the direct impact is elastic, such a reflected ion appears experimentally to have experienced an inelastic collision.

IV. TRANSITIONS INVOLVING NEGATIVE IONS

For the sake of completeness processes involving negative ions are mentioned here. In the vicinity of a metal surface, a neutral atom may capture a metal electron to form a negative ion or a negative ion may lose its electron to the metal. These resonance transitions can be treated in the same way as the neutralization and ionization processes already described. Modification of existing theory by the inclusion of image potential leads to the specification of ranges from the surface where transitions may take place. It can be shown, for example, that a negative ion may be formed near a surface even if the electron affinity of the atom is less than the work function of the surface. In such a case the negative ion may lose its electron in moving farther away from the surface. In so doing, it will lose kinetic energy equal to the difference in image potential at the two distances. Such a collision with the surface appears experimentally to be inelastic.

V. METASTABLE DE-EXCITATION MECHANISM FOR SECONDARY ELECTRON EMISSION (He^+ ON Mo)

As already mentioned in Sec. I, the He^+ ion is assumed[1,2] to neutralize to the $He(^3S_1)$ metastable state while approaching the surface. At closer approach, the metastable atom is assumed to de-excite by capturing a metal electron into the ground atomic state and ejecting a $2s$ atomic electron. The analysis of this case in this section differs only in detail from those involving other singly ionized rare gas ions on many metals.

Cobas and Lamb[2] have calculated both stages of this process for He^+ on Mo. The first stage [He^+ to $He(^3S_1)$] will be of principal interest. This calculation involves a matrix element which is essentially an overlap integral of the initial and final wave functions of the system. The transition probability is proportional to the product of the square of the matrix element and the energy density of final states.

When the image potential involved in the transition [He^+ to $He(^3S_1)$] is neglected, $V_i - V_e = 4.77$ ev exceeds $\phi = 4.27$ ev by 0.5 ev to satisfy Eq. (1). No other state satisfies this condition. Since Cobas and Lamb did not take into account the image potential, they took the energy density of final states appropriate to infinite separation of the ion from the surface. As can be seen from Fig. 3 the density of final states becomes zero for $s < s_0 = 7$A. Thus the Cobas and Lamb calculation is correct only for distances greater than s_0. If He^+ has not undergone a transition to the metastable state by the time it approaches s_0, it cannot neutralize in its approach to closer distances. From Cobas and Lamb's calculation, it can be shown that only a small fraction of He^+ are neutralized in the approach to s_0 even if the ions possess thermal velocities. For faster ions, a very much smaller fraction will be neutralized in the approach to s_0.

When the newly formed metastables approach closer than s_0, Fig. 4 shows that the density of final states for ionization becomes very large. The matrix element for ionization [$He(^3S_1)$ to He^+] is the same as for neutralization [He^+ to $He(^3S_1)$] since initial and final states are interchanged. Thus Cobas and Lamb's matrix element may be used to calculate the probability for ionization of a $He(^3S_1)$ metastable atom at distances less than s_0. A computation shows that the probability of a metastable approaching $s = 2$A without being ionized is exceedingly small even for kinetic energies of 1000 ev. Cobas and Lamb were able to show that if a metastable beam is incident on a surface the metastable de-excitation process occurs with appreciable probability only for $s \lesssim 1$A. Since metastables are almost completely ionized at distances greater than 2A, it is clear that the contribution to secondary electron emission by de-excitation of approaching metastables in the range greater than 2A is very small.

What happens at distances less than 2A is more difficult to predict with certainity. As noted in Sec. II, a simple consideration of ionic and atomic "radii" shows that a recrossing of potential curves is not expected. The possibility that a small fraction of the ions may be neutralized in a rather limited range cannot be excluded as detailed knowledge of the surface repulsive potentials is lacking. Any excited atom so formed must de-excite very rapidly if it is to give rise to a secondary electron; otherwise the rebounding atom will be ionized again after moving away a very short distance. The rather severe limitations imposed by this analysis lead one to believe that very few secondary electrons result from this process and that the main body of secondary electrons arise in some other manner.

If such processes are neglected for the moment, the rebounding ion may again become neutralized after it has traveled past s_0. Whether it emerges as an ion or metastable depends upon the integrated transition probability for neutralization from s_0 to infinity on its outward trip. It thus appears that whether a reflected particle is a metastable or ion depends not on what happens in an approach to the surface, but on what happens when it travels away. It can be seen that if the approaching particle had been a metastable, the results would be the same since it becomes an ion at close approach. Thus, it appears reasonable that the composition of a reflected beam of particles is independent of whether the incident particles are ions or metastables.

Cobas and Lamb's[2] theory requires that a beam of ions be nearly completely transformed to a metastable beam on approach. In order to explain Oliphant's[5] observation of both reflected ions and metastables, Cobas and Lamb postulated that a metal electron oscillates rapidly between the ion and the metal, the number of such oscillations determining the identity of the reflected particle. The present theory eliminates the need for this mechanism.

VI. THE AUGER PROCESS FOR SECONDARY ELECTRON EMISSION

Shekhter[4] has proposed an alternative process to explain secondary electron emission. The system of metal plus ion de-excites itself in an Auger type process by the simultaneous transition of two metal electrons; one to the ground state of the atom and the other to the continuum appearing as a secondary electron. According to Shekhter's calculations, the Auger process is most important for very close approach (of the order of 3A or less). Shekhter calculated the secondary electron yield to be 0.10 per incident ion for 20-ev ions. The theory requires the yield to be inversely proportional to ion velocity. This dependence is not borne out by experiment. Hagstrum's[6] measurements of secondary electron yield by He^+ on atomically clean Mo surfaces give a value of 0.25 for secondary electron yield relatively independent of ion energies between 10 and 1000 ev. Although this difficulty exists for the Auger process, it appears less subject to criticism than does the metastable mechanism.

It appears likely that a beam of metastable atoms will be largely ionized at distances greater than that for which the Auger process has an appreciable probability. Thus, secondary electron yield by metastable atoms should be nearly identical to that by ions.

VII. CONCLUSION

A potential curve method has been developed for describing resonance transitions involving atoms and ions in close proximity to metal surfaces. The effect of image potential on the energy levels of the system limits transitions to definite ranges of separation from the surface. It is found that Cobas and Lamb's[2] calculations of the ion to metastable [$He^+ \rightarrow He(^3S_1)$ at a Mo surface] process are seriously in error. Further, it has been shown that any contribution to secondary electron emission by the de-excitation of metastable atoms is very small. It is believed that an Auger type process is is responsible for most of the secondary electrons.

The author wishes to thank the members of the Physics Department of the Westinghouse Research Laboratories for many interesting discussions, suggestions, and criticism of this work. The author is particularly indebted to T. Holstein, who showed how the potential diagrams should be constructed and contributed many valuable suggestions.

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