Section V
Electron emission
Principles and mechanisms of ion induced electron emission

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The mechanisms responsible for emission of electron from solids are described, separating them, when possible, into electron excitation, electron transport and cascade multiplication, and transmission through the surface barrier. Discussions include important energy quantities and quantum mechanical effects in the transport of slow electrons in the solid and through the surface barrier. Some new aspects not previously described are explored, such as how much information can be obtained by treating insulators as dense gases, electron loss from the projectile, differences between prompt and delayed excitation processes and final state effects in multiple electron emission.

1. Introduction

Electron emission (EE) is one of the most conspicuous consequences of inelastic ion-surface collisions and, in general, of interactions of any ionizing radiation with condensed matter. It is basically understood as follows: the primary particle, the ionizing projectile, frees secondary electrons in collision events. These electrons then undergo a cascade of collisions in the solid, which can produce additional ionization, until their energy is degraded into heat or stored in long-lived excited states. Those excited electrons which are directed outwards can cross the surface of the solid and escape before being thermalized, giving rise to secondary EE. The main observable in EE is the average electron yield \( \gamma \) (number of electrons ejected per primary particle), either as an integral quantity or in the form of distributions of electrons according to their energies, angles of emission, and spin state. EE events are statistically distributed; that is, the yield fluctuates around the mean value \( \gamma \) and is described by probabilities of emission of \( n \) electrons per projectile.

Experiments involve measuring the dependence of EE on different factors. These include the type of projectile and the target and the experimental geometry. The most important projectile properties are the type (heavy particle, electron, photon, etc.) and the energy. For heavy particles, additional important properties are also their excitation and ionization state, their mass, and whether they come as single atoms, molecules or clusters of molecules. Relevant target properties are the elemental composition and atomic and electronic structure in the surface region, the magnitude of surface electrostatic fields (for insulators and semiconductors), the temperature, and, for magnetic materials, the degree of magnetization. The relevant geometrical factors in the experiment include the angle of incidence with respect to the surface and to possible preferred crystallographic planes. The achievable reproducibility of EE yields from clear surfaces shown in fig. 1 is quite high compared with data from other ion-surface collision experiments.

The topic of ion induced EE has been surveyed recently with emphasis on observations [1–3] and theory [4–6] and discussed at a specialized conference [7]. Here, I will describe the main physical processes in kinetic electron emission (KEE) from solids, that is, EE induced by the motion of heavy atomic and molecular projectiles. Potential EE (PEE) which results from conversion of the potential energy of the projectile without need for atomic motion will not be described in detail; the topic has been covered in another set of recent reviews [8–12]. I will describe KEE from a different perspective, touching some aspects not previously considered. The starting point of this work will be a discussion of individual scattering events in gases and what can be expected by considering the solid as a dense gas, emphasizing similarities and differences.

2. Gas-phase versus ion–surface collisions

EE from surfaces is the counterpart of ionization in gas-phase collisions (although not all processes which produce ions librate free electrons). Much insight can be gained by studying ionization in the gas phase, since the mechanisms occur directly, or in a modified form, in ion–surface collisions. Similar considerations should also apply to collisions with large molecules and with clusters. Ionization collisions take the form of target ionization, projectile ionization (electron loss or detachment), and combined processes. Ionization by
Fig. 1. Total electron yield $\gamma$ for $H^+$ impact on clean metals as a function of ion energy. The data has been obtained at five different laboratories: $\circ$ - Baragiola et al. [29], $\bullet$ - Hasselkamp et al. [141], $\times$ - Veje [142], $\cdots$ - Holmén et al. [143,144], $\Box$ - Koyama [145], $\ldots$ - interpolation between data sets (from Hasselkamp [146]).

heavy particles can also accompany other processes, such as charge exchange, excitation, and dissociation. Ionization can occur during the collision, or after delayed relaxation of excited atomic states, such as in autoionization or Auger processes.

In dense gases and solids, energetic electrons released in the primary ionization events can produce additional ionizations by colliding with other atoms, generating a collision cascade which dilutes the energy initially concentrated in the projectile into a large number of particles. The observation of EE events in gases and solids implies the collection of part of the electrons in the cascade before they recombine with positive ions. In targets with an excitation gap (gases and nonmetallic solids) this can be done with collectors inside or outside the target material. In metals, the observation of ionizations has been restricted to electron ejection from the surface.

All collision processes will be different in gases than in condensed matter, due to differences in the initial and final electronic states. However, some of these differences are small and so one can draw general analogies as a heuristic approach to understand EE in solids. From there one can then discuss specific condensed matter effects and evaluate their importance.

2.1. Gas targets

Let us consider first a particle of energy $E_0$ passing through a chamber containing gas at density $N$ where electrically biased electrodes are used to separate and collect ions and electrons. One can distinguish between experiments done at low pressures (thin targets in single-collision conditions) and at high pressures (thick or dense targets). For thin targets, the probability of double collisions is small; i.e., there is no significant change in the state of the projectile or scattering of the ejected electrons on their way to the collector. The number of ionization events per unit path length $dx$ in the gas, and per projectile is:

$$\frac{d\nu(E_0)}{dx} = \sigma(E_0)N,$$

where $\sigma$ is the ionization cross section.

By increasing the gas pressure sufficiently, one can already discern several specific molecular and condensed matter effects. Projectiles will suffer multiple collisions some of which may produce several sequential and, possibly, simultaneous ionizations. Furthermore, the projectile will lose energy and may change its electronic structure, be deflected and set target atoms in motion. These target recoils can produce additional ionization by conversion of their potential or kinetic energy.

The electrons ejected in primary ionizations, the first-generation (1G) electrons will undergo a variety of collision events after being ejected. They will scatter and lose energy in collisions with target molecules; some of these collisions can produce additional ionization if the electron energy is above the ionization potential of the target. When the energy of the electrons degrades to a few eV or less, they can be lost by recombination with ions or by attachment to target species to produce negative ions.

By applying an electric field to the gas, the charges can be separated before significant recombination occurs, collected, and counted. An important empirical finding is that $d\nu/Ndx$ is equal to the electronic stopping cross section $S_e = (dE/N \, dx)_e$ divided by a constant, $w$:

$$\frac{d\nu(E)}{dx} = S_e/N/w.$$

If the particle stops completely in the gas, the number of ion pairs produced is:

$$\nu = \int_0^{E_0} \frac{S(E)_e}{S(E)_{\text{tot}}} \frac{1}{w} \, dE,$$

where $S_{\text{tot}}$ is the sum of the electronic and the nuclear (elastic) stopping cross sections. If $E_0$ is sufficiently large, $S_{\text{tot}} \sim S_e$ over most of the path and one can use the asymptotic expression:

$$\nu \approx \frac{E_0}{W}.$$
The average energy required to produce an ion pair, the "W-value" depends very little on the type and energy of the ionizing radiation and relatively little on the nature of the gas [13,14]. This property is very important in the operation of the gas-filled proportional counter [15], a radiation detector used to analyze the energy of the incident radiation by counting the number of ion pairs produced.

At low impact velocities, \( v \) is no longer proportional to projectile energy [16,17] since the fraction of the projectile energy available for electronic excitations decreases due to the generation of energetic target recoils and atomic vibrations in elastic collisions with target nuclei. Some of the energy transferred to the recoils will still be delivered to the electronic system in additional ionization collisions [18,19]. The relative contribution of recoils increases with increasing ratio of the mass of the projectile to target atoms. This recoil effect has important implications in KEE at low energies. An additional effect occurring as the excitation energy approaches the ionization threshold, is a fall of the average energy of the excited electrons, so that fewer can produce secondary ionizations.

The number of ion pairs produced is statistically distributed, since there is a fluctuation of energy transfers in individual collisions. The fluctuations in \( v \) are important because they determine the energy resolution of proportional counters (and solid state radiation detectors). It has been found that fluctuations are not those corresponding to a Poisson distribution. Rather, the variance is \( s^2 = Fv \), where \( F \) is the Fano factor [20]. Table 1 gives values of \( W \) and \( F \) for some gases and also some liquids and semiconductors [15]. \( F \) should increase near the ionization threshold to the value \( F = 1 \) resulting from a Poisson distribution [21,22].

2.2. Solids

The concept of mean energy to create an ion pair is well defined in semiconductors and insulating solids, where one usually speaks in terms of electron–hole pairs. Like in gases, \( W \) can be measured by separating the charges in an electric field, and collecting them in electrodes, before significant recombination occurs. Some loss of charges occurs when the density of ionization is very high (e.g., for fast, heavy projectiles such as fission fragments).

Ionization of semiconductors is usually studied through induced electrical conductivity in the bulk [23–25] and at surfaces [26,27]. It has important application in radiation detectors and in the behavior of electronic components in space. Studies in insulators and more complicated due to, in general, a low mobility and high trapping rates for electrons and holes. Slow or trapped charges will help set up high internal electric fields which will hinder or impede charge collection. In the case of high mobility insulators, such as diamond or liquid Xe, the collection of induced charge is more feasible and has led to the development of practical radiation detectors. In the case of metals, charge separation is not possible, and the "number of excited electrons" is not a clearly defined quantity due to the possibility of fast and continuous energy degradation. Such behavior is understood diagramatically in fig. 2.

Some condensed matter effects, already found in molecular targets, occur when the distance between target atoms becomes very small. A small distance between ions at high ionization densities will cause considerable repulsive forces. They can dissociate free molecules and dislodge the lattice in solids, creating a damage track along the path of the projectile [28]. The high ion concentration will also set up a high electric field which will affect the motion of the electrons and holes. The creation of high ionization densities has not been studied; one can expect saturation effects in the region close to the maximum of the stopping cross.
section, especially for highly charged projectiles. One of the important unsolved questions is the probability of exciting plasmons in the presence of a plasmon field previously excited by the same projectile.

Quantum effects appear in the ionization cascade when the distance between atoms is small. The associated de Broglie wavelength \( \lambda = h/mv = 12.25 \, \text{Å} \, E^{-1/2} \) (eV) for low energy cascade electrons is of the order of or larger than the nearest neighbor distance between atoms in molecules and condensed matter. Coherent scattering and interference of scattered waves will occur which, in the case of an ordered array of target atoms, will result in diffraction patterns.

The other important aspect of the solid is the abrupt discontinuity of the surface. This interrupts the full development of the cascade, a fact not considered or described in many transport theories. This interruption allows EE which would not be observable otherwise. The surface barrier hinders ejection of those electrons that have fallen below the vacuum level due to energy loss collisions. Those electrons will be attenuated in number with a probability that depends on the distance between the point of excitation and the surface. Thus, both the existence of a surface barrier and inelastic collisions of cascade electrons serve to determine a mean escape depth, \( L_e \), from which electrons can originate.

By analogy to the situation in gases, one can thus expect a proportionality between the electron yield \( \gamma \) and \( \epsilon \), the energy deposited in electronic excitations within the escape depth. Experiments have shown that this proportionality holds over a wide range of conditions. In many cases involving fast projectiles, \( \epsilon \propto S_r N L / \cos(\alpha) \), where \( \alpha \) is the angle of incidence of the projectile with respect to the surface normal. We have found [29] a fairly universal proportionality of electron yields with the electronic stopping power, \( dE/dx \), rather than with the stopping cross section \( dE/N \, dx \), a quantity usually preferred due to its insensitivity to target density:

\[
\gamma = B (dE/dx)_e / \cos(\alpha). \tag{5}
\]

Deviations from this formula are expected, and observed, at low energies, at large angles of incidence, in conditions of strong ionization by recoils and when the electronic cascade is highly anisotropic. I prefer not to consider \( B \) as a “material parameter” in the sense of Schou’s \( \Lambda \) [30], since the properties of the cascade and the probability of escape depend, in principle, also on the projectile through the angular and energy distribution of 1G electrons. In practice, it is observed that in some cases, \( B \) seems to be relatively independent of the target material and in others to depend on the type of projectile. We found that \( B \) falls in the narrow band: \( B = 0.10 \pm 0.03 \, \text{Å} / \text{eV} \) for different clean metal targets under 5–50 keV \( \text{H}^+ \) bombardment [29] and about 20% lower for heavier ions (He through Ne) [31]. Hasselkamp et al. [32] found that these values of \( B \) also hold up to 800 keV and extended the observations to 27 metals and semiconductors. They found that the band included most materials with the exception of Mg, Cd and In which fall above and Cu and Nb which fall below the band. They also found that \( B \) for Ar impact is about 20% lower and does not show the general constancy with velocity found for incident \( \text{H}^+ \) [33]. \( B \) values around 0.31 eV/Å have been found for the total yields from C foils bombarded by fast ions ranging from hydrogen to uranium [34–36].

3. The primary processes

The EE process is conveniently divided into three steps, (1) primary ionization, (2) electron transport, and (3) escape through the surface, except when excitations occur just at the surface, when the three events are inextricably coupled.

3.1. Electron excitation

The most important step in EE is the primary ionization. The effect of the electron cascade and the surface barrier may be minimal for excitations outside surfaces, but the ionization event must always occur in EE. There are several ways in which the projectile can transfer energy to target electrons. Direct, “prompt” processes occur during the collision, in a short time scale 0.01–2 fs. Indirect, “delayed” processes result from the relaxation of electronic energy stored during the collision. The time scale of these processes is 0.1–1 fs for plasmon decay, 1–100 fs for Auger decay [37,38] to seconds or longer for exoelectron emission after particle impact [39].

3.1.1. Direct processes

The minimum or threshold energy required to liberate an electron from a perfect solid, \( U \), is the energy difference between the top of the valence band and the vacuum level. This is the work function in metals, \( \phi \), and the electron affinity \( \chi \) plus the band gap \( E_g \) in insulators and semiconductors. Thus, \( U \) is equal to the photoelectric threshold of the surface. At finite temperatures, EE can occur below this threshold, from occupied states lying above the valence band maximum. Threshold energies range from 2.1 eV for Cs to more than 20 eV for condensed He. I introduce here a measure of the efficiency of the EE process, the quantity \( Q = E_d / \gamma \), the average energy spent to emit an electron, where \( E_d \) is the electronic energy lost by the projectile in the escape region. \( Q \) can be delivered by the projectile in different ways. If the projectile is excited or ionized, it carries an internal potential en-
energy $E_i$ that can be released by multiple electron interactions, like in the Auger process. If $E_i > 2U$, potential EE can occur. In this case, values of $Q$ range from $\sim 30$ eV at low excitation energies [40] to $90$ eV and more for multiply-charged projectiles [41,42]. In the case of KEE, $Q \sim 300$ eV for clean metals and semiconductors [29,31,32] and approximately the $W$-value for thin Ar films [43].

The contribution of PEE yields $\gamma_p$ to KEE can be deduced in different ways. Comparison of EE by ground state neutrals and ions show that the difference in the yields remain approximately constant in the keV energy range, suggesting a constancy in $\gamma_p$ with ion velocity $v_0$ [44]. On the other hand, Hagstrum [45] has shown that in many cases PEE depends on $v_0$ due to competition of different PEE processes depending on the interaction time of the ion at the surface or on the normal component of $v_0$. A strong energy dependence is found for molecular ion impact on surfaces, where the internal energy might be dissipated in molecular breakup, depending on the ratio between the transition rates for Auger processes and dissociation [46]. A method has been proposed that uses emission statistics to separate PEE from KEE by assuming that PEE cannot produce more than one electron [47], i.e. for $E_i > 3U$, when the excited electron cannot produce additional EE. However, the situation is not clearly defined since the KEE threshold for emission of one electron is probably different from that for emission of two electrons.

3.1.1.1. Kinetic electron emission There are several ways in which moving projectiles can excite electrons at the expense of their kinetic energy. At high velocities, the energy transfer can be a result of a close collision with a target electron, and is described by the Rutherford cross section. It can also result from distant collisions, where the transient electric field produced by a passing charged projectile induces a dipole excitation. The perturbation can be described as a source of virtual photons with excitation rates related to photoabsorption cross sections [48]. At lower velocities, it is also necessary to take into account electron-electron interactions. When the velocity is very low, the electrons can follow the perturbing effect of the ion adiabatically, and excitations are very unlikely. The angular distribution of electrons ejected in gas-phase collisions is usually forward peaked, especially for the more energetic electrons which result from direct binary collisions with the projectile.

In the treatment of EE from metals under slow ion impact problems arise when using the free-electron model to describe the solid. This model is often a good first-order approximation of the valence band; for instance, stopping power calculations using electron gas models provide generally good agreement with experiment. The free-electron model was first tested by the author and co-workers for Al bombarded with ion of velocities $v$ lower than the Fermi velocity $v_F$ (fig. 3) [31]. For free electron targets, KEE is limited by momentum conservation due to the strong mismatch between the masses of the electron, $m$, and of the heavy projectile, $M$. The maximum energy transfer to an electron occurs when an electron at the Fermi surface, with momentum antiparallel to the projectile, scatters into a final state with momentum parallel to the projectile. It is given by:

$$E_{\text{max}} = 2mv(v + v_F).$$

The excited electron is directed inwards but can be
The experimental data show that the yield curves extrapolate to zero for velocities close to this value for light ion impact, if one subtracts the contribution of PEE. Lower thresholds can be obtained if one takes into account phonon exchange with the lattice, e.g., unkllap processes, or if the collision occurs in the proximity of ion cores in the solid [50] where the valence electrons have higher velocities.

However, heavy ions are found to produce KEE at much smaller impact velocities. This situation reminds us of the problem of the photoelectric effect from metals, where emission occurs even though a photon cannot be absorbed by a free electron. The conservation laws are fulfilled by the participation of a target atom in the exchange of momentum. Thus, we inferred that KEE at low velocities requires a relatively close atomic collision. This implies the same excitation mechanism for metals and nonmetals and makes it unnecessary to invoke inner-shell excitations [51].

The need for close atomic collisions suggests that the ground state band structure of the solid is not important during excitation. This would then allow us to use atomic excitation models, such as Firsov's friction model of energy transfer in slow collisions [52]. In this model, excitation occurs when electrons flow between the two atoms during encounter, changing their net average momentum. This builds up excitation energy which can cause ionization when it exceeds the ionization potential. Firsov's theory was developed using statistical atomic models, and has not yet been fully justified. It has been applied with limited success to describe stopping powers [52]. We recognized that this would allow the description of KEE induced by slow heavy ions, and applied it to describe experimental data at low energies and to establish quantitatively the contribution of ionizations due to recoiling target atoms [31,53]. That KEE requires close collisions with target atoms has been recently demonstrated by Rabalais et al. [54], who studied the impact parameter dependence of Ar induced KEE from Ni(110) at 4 keV. They observed essentially no emission at grazing incidence and emission started abruptly when the decreased shadowing of atomic planes allowed the minimum impact parameter in a collision to be below 0.3 Å, or about the sum of the maximum radial charge density of the L-shells of Ar and Ni.

3.1.1.2. Electron emission from the projectile In an atomic collision, the excited electron may originate not only from the target atom but also from the projectile. To estimate the contribution of electron loss to KEE, I have used gas-phase cross sections, which are similar to those for target ionization (electron loss is target ionization in the projectile reference frame). If the projectile beam is charge equilibrated, the number of electron lost by the projectile is given by \( \nu_1 = \sigma_e N_x \), where \( \sigma_e \) is the cross section for a charge exchange cycle [55]. For a beam consisting of singly charged ions and neutrals, \( \sigma_e = \sigma_{10} / (\sigma_{10} + \sigma_{01}) \), where \( \sigma_{nm} \) is the cross section for a collision that changes the charge of the projectile from \( n \) to \( m \). If the projectile beam is initially neutral or if it becomes neutralized immediately upon entering the solids, \( \nu_1 = \sigma_{01} N_x \). Electron recapture by the ionized projectile usually occurs too deep in the target to be a source of electrons in a further electron loss event, except in insulators or in the case of nonmetals.

![Figure 4](image.png)

Fig. 4. Fraction of electrons originating in electron loss from the projectile and electron multiplication factor for collisions of charge equilibrated H beams with Ar.
of the downstream side of foils. If the electron is emitted isotropically in the projectile frame, it will have an average energy \( E_{\text{eq}} = (m/M)E_0 \) in the laboratory system. This will produce a forward peaking which is noticeable if \( E_{\text{eq}} \) is more than a few eV. During the collision, a loosely bound projectile electron, like in negative ion or in Rydberg states, will have a stronger interaction with the target atom than with its parent core. It will then scatter approximately as a free electron and ionize easily for \( E_{\text{eq}} \) larger than its binding energy.

I have estimated the contribution of electron loss to KEE for proton impact on Ar films by using gas-phase cross sections [56–58]. In thick films, we can assume that the ion beam is charge equilibrated through many charge exchange cycles over most of its path. In this case, we show in fig. 4 a \( \sim 30\% \) contribution of electron loss at low energies falling rapidly with energy after the maximum in the electron capture cross section. In the case of neutral H impact on thin films, where charge exchange cycles are not important, the contribution of electron loss is larger; it grows with energy from 35\% at 10 keV to 62\% at 1 MeV.

### 3.1.1.3. Molecular effects in KEE

An interesting question is how the KEE yield produced by molecular ions compares to the yields produced by its constituent atoms. It is found that for hydrogen projectiles, the ratio of yields \( R_1 = \gamma(\text{H}_2^+, v)/2\gamma(\text{H}^+, v) \) at equal velocity is \( R_2 < 1 \) at low energies and \( R_2 > 1 \) at energies higher than about 100 keV/proton [3,59–62]. The reduction at low energies occurs even taking into account a smaller PEE by molecular ions [8]. The origin of this molecular effect has been a matter of controversy. We have argued for an interference effect, which has been demonstrated for stopping powers: molecular ions lose less energy than protons at low velocities and more at high velocities. This is due to an interference in the scattering of the target electrons in the molecular system [63]. At high velocities where the dynamic screening is weakened, the two protons act like a He\(^{2+}\) ion in distant collisions and give a higher yield due to the \( z^2 \) dependence of the energy losses. Additional emission will also result from loss of the H\(_2^+\) electron.

An alternative view [64] proposed that the molecular fragments act totally independent of each other: \( \gamma(H_2^+) = \gamma(H^+) + \gamma(H^0) \) (i.e., interference effects are ignored) and explains \( R_2 < 1 \) at low velocities by assuming that \( \gamma(H^+) < \gamma(H^0) \). This assumption is based on the lower stopping power for H\(^0\) compared to H\(^+\), caused by screening of the proton charge in H\(^0\). However, screening affects principally the low energy loss contributions to the stopping power, which are relatively unimportant in exciting electrons above the vacuum level. Furthermore, ionization cross sections at keV energies may be larger for H than for H\(^+\) impact [65]. A complete description of the molecular effect must necessarily include the (velocity dependent) contributions of interference during excitation, electron loss, and screening effects in ionization rates.

### 3.1.2. Delayed processes

Energy stored temporarily in inner-shell holes or plasmons can be later released in energetic electrons which can produce additional ionizations. One of the main properties of these temporary energy stores is that the energetic electrons produced from them will tend to have an isotropic angular distribution, unlike electrons from direct energy transfers, which tend to peak in the forward direction. The different angular distributions will affect the electron transport and thus the KEE yields.

#### 3.1.2.1. Emission from Auger decay

Holes in shallow inner (core) atomic levels usually decay by the emission of Auger electrons, easily identified in the high energy tail of the energy distribution of ejected electrons (fig. 5 [66]). The emission is delayed with respect to excitation, by the lifetime of the core hole (typically 1–10 fs). The subject of ion induced electron emission is covered in several reviews [8,67–69]. Core excitations can occur in the projectile and in the target atom, as a result of small impact parameter collisions. The Auger decay can occur in the bulk or in vacuum for reflected projectiles or sputtered atoms. Auger energies will be different in both cases, and reflect the different distribution of valence electrons at the location of the core hole. There are several instances of misconceptions in the literature regarding the ejection of core-excited atoms. Although the violent collisions often produce sputtering as well, the inverse is not true; that is, most sputtering events are not accompanied by inner-shell excitations. Therefore no direct correlation should be expected between Auger and sputtering yields. The Auger decay of excited heavy projectiles in vacuum can

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**V. ELECTRON EMISSION**

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![Electron Energy Spectrum from Impact of 2 keV Ne\(^+\) on clean Mg surfaces](image-url)
produce high mean charges of projectiles that have traversed thin foils [70–72], or backscattered from the solid [66,73]. Auger emission from target atoms can produce high ion yields in secondary ion mass spectrometry.

Auger energy distributions consist of a broad structure, readily associated to Auger transitions in the bulk, and sharp (1 eV wide or narrower) atomic-like peaks. Analysis of Doppler shifts and broadenings of the sharp lines [74,75], and the observation of energy shifts which accompany work function changes induced by alkali adsorption [76] have shown that they correspond to transitions in core-excited sputtered atoms decaying in vacuum. To first order, Auger emission in vacuum is isotropic while that from the bulk follows a cosine law. This causes the ratio of intensity of atomic Auger lines to bulk lines to be strongly enhanced for emission close to the surface [77]. Very detailed studies of the dependence of ion-induced Auger spectra on angles of incidence and emission have just been published [78].

A topic still subject to controversy is the relative role of core excitations in collisions between the projectile and a target atomic (pt) to those between two target atoms (tt). Here the evidence is indirect, and comes from comparison of experiments to computer simulations, which have reached a high degree of development. Our Monte Carlo analysis of Be K emission [79] showed an excellent agreement with the experimental energy dependence of the Auger yield. This provided firm grounds to determine the relative importance of pt and tt processes in X-ray emission yields, more accurately than possible using analytical theory. The results show that tt collisions dominate EE by Auger processes at the lower energies. Recent simulations of L-shell excitations in bombardment of solid Al targets with Ar ions [80] conclude that pt collisions are largely responsible for Auger yields even at energies close to the threshold. This is in striking contrast with other recent theoretical studies [81–83] and is also contradicted by the observation that Auger yields in Al [84] and Si [85] compounds vary with the square of the concentration of the light element which is excited. Detailed measurements by Bonanno et al. [86] have recently confirmed that the ratio of pt to tt contributions increases with increasing energy and also varies with incidence angle.

The origin of the continuum tails extending below the Auger peaks in the region of very high electron energies is still obscure. At high impact velocities, they have been explained to arise from binary collisions between the projectile and a target electron. At low velocities, the explanation is still a matter of debate [87], models proposed include direct coupling to the continuum and emission of Auger electrons during the collision. Our measurements for very low energy (0.5–6 keV) ions in solids have shown that the continuum electron energy distributions extend up to a surprisingly large fraction of the center-of-mass energy (fig. 6) [88]. This shows that the extremely high electron energies result from nearly head-on collisions between the projectile and a target atoms. The high energy tails are strongly dependent on the type of target, they decay generally slower with electron energy the higher the atomic number of the target.

3.1.2.2. Plasmons Plasmons are collective excitations of the electrons in the form of charge density fluctuations with frequency \( \omega_p \). They can be excited in surface and bulk modes by particles with velocities larger than about \( v_F \) or by the sudden creation or annihilation of a core hole. Plasmons can also be generated by the energetic electrons in the cascade created by ions slower than \( v_F \) [89].

The delocalized plasmon oscillations can decay by localizing into a single electron–hole pair. It has been found that this localization occurs at a very short distance from the point of excitation [90,91]. The electron resulting from plasmon decay can be detected in the energy distribution of ejected electrons as a broad bump. This results in a maximum electron energy of \( h\omega_p \sim U \) outside the solid, plus a broadening resulting from the finite plasmon lifetime. This lifetime cannot be explained within free-electron gas models, but is related to the real band structure of the solid. Plasmons have been found to contribute more to EE than the direct transfer of the same amount of energy into electron–hole pairs [92,93], under excitation with high energy electrons. Similar behaviour is expected for high velocity ions. This effect has not been taken into account in current EE models.
3.2. Electron transport

A proper description of the cascade requires knowledge of the probability that a 1G electron loses energy and eventually generates new excited electrons. This problem has been studied by using an electron gas model to describe inelastic electron-electron scattering. In some cases, simulations have included classical electron trajectories using Monte Carlo methods between elastic scattering events with single atoms [94]. The justification for doing this has not been given. The problem is that the majority of the electrons in the cascade have wavelengths of the order of larger than the mean atomic spacing, a. The electrons will not, therefore, interact in a binary fashion with a single atom at a time, and the concept of cross section cannot be applied as is done in classical transport theory or simulations. Diffraction and interference of very low energy electrons is observed for instance in extended X-ray absorption fine structures (EXAFS) [95].

A different question is whether the trajectory of an electron can be defined between elastic scattering events. A classical description is valid if the uncertainty in the momentum $\hbar/a$ due to localization within a region of size a is much less than the electron momentum $p$. This implies the often fulfilled condition $E' \gg 0.5$ eV far from the Brillouin zone boundaries, where $E'$ is the electron energy inside the solid.

An important consideration in understanding electron transport is that the probability of a small inelastic energy loss is very small for low energy electrons [96]. This is because all the states of the valence band are occupied so that only the top of the band can absorb small energy transfers. Fig. 7 shows the probability that an electron loses energy above a given value in carbon [97]; it can be seen that the most probable energy loss is slightly larger than the energy of a bulk plasmon (~ 25 eV). A large average energy loss means that an inelastic interaction will most likely attenuate secondary electrons (drop their energy below the vacuum level). This in turn means that secondaries suffer very few inelastic collisions before they escape. Therefore, the randomization of their motion in the cascade should occur mainly be elastic scattering or quasi-elastic scattering with phonons. In nonmetals low energy losses are more strongly suppressed; only losses larger than the band gap are allowed, neglecting excitons and other gap states.

At intermediate and high energies, a substantial fraction of the secondaries will have enough energy to produce additional EE by cascade multiplication. The extent of the cascade will be determined mainly by the range $R(E')$ of the 1G electron, which is a function of its energy $E'$. $R$ is defined here as the mean distance it travels from the excitation site before its energy falls below the vacuum level. The shape of the cascade will be mainly determined by the angular distribution of the 1G secondaries. For fast light projectiles, this distribution of the secondaries is strongly peaked forward, the more so the faster the projectile and the faster the ejected electron [98]. The anisotropy of the primary event will tend to be washed out by elastic collisions.

Cascade multiplication depends on the electron energy and can be described by a factor $\mu$ equal to the total number of electrons divided by the number of 1G electrons. The probability that a 1G electron produces at least one more electron above the vacuum level is zero if the energy above the vacuum level is less than twice the threshold energy, i.e., $E < 2U$. Based on pair production in gases, an approximate multiplication factor for electrons will be given by $\mu(E) \sim 1 + (E - U)/U$. Thus the transition from the single excitation to cascade multiplication regime will depend on the energy distribution of the excited electrons. One can get information about this in the case of gases, where one knows the primary ionization rate, $\sigma_i N dx$ and total ionization rate $S_e N dx/W$. The multiplication factor is then given by:

$$\mu = S_e / \sigma_i W.$$  

Fig. 4 shows the multiplication factor $\mu$ for protons in Ar, taking into account also charge changing collisions, calculated using gas-phase data from the literature [99]. One can see that at 10 keV a small fraction of the ionizations is caused by secondary electrons, whereas at high energy, more than half of the excited electrons are produced in the cascade.

The diffusion of the deposited energy away from the collision site causes the number of excited electrons to vary with the distance to the surface, even if the scattering and energy loss of the projectile can be...
neglected [6,100,101]. This is because at depth \( z > R \)
(the electron range) there are contributions from the
region extending from \( z - R \) to \( z + R \), whereas at the
surface, there is only a contribution from the region extending
from \( z = 0 \) to \( z = R \).

A depth dependence of the deposited energy can be
caused by a change in the charge of the projectile as it
enters the solid [102], which will also result in a dependence
of KEE on the charge of the ion. At low velocities, energy degradation of the projectile in the elec-
tron escape region becomes important. This, by itself,
causes a decrease in the primary ionization density
with depth which may be compensated by the increase
due to larger path lengths produced by angular scattering
and ionization by recoils. This latter contribution
may increase or decrease with energy, depending on
the projectile-target combination [30].

To calculate how many electrons reach the surface,
we recall that when an inelastic energy loss occurs, it is
usually a substantial fraction of the electron energy.
The flux of electrons which reaches the surface with
final electron energy \( E' > U \) can then be approximated
by the flux of electrons which have not undergone an
inelastic event. The probability of attenuation is de-
scribed by the inverse of the inelastic mean free path
\( \lambda_{\text{in}} \). If the probability for elastic scattering is small,
such as at high electron energies or for low \( Z \) targets,
the electrons are attenuated in straight paths to the
surface, according to the attenuation length [103]:

\[
L = \frac{\lambda_{\text{in}}}{\cos \theta'},
\]

where \( \theta' \) is the angle of the internal path with respect
to the surface normal. The formula should hold in only
few cases. For instance, Monte Carlo calculations by
Dehaes et al. [104] for proton impact on Al above 10
keV show than an electron suffers, between birth and
escape, an average of about 7 elastic and 0.4 inelastic
collisions. In the more usual case where elastic scatter-
ing dominates, the diffusion process will be described
by an attenuation length [100]:

\[
L = \left( \lambda_{\text{tr}} \lambda_{\text{in}} / 3 \right)^{1/2},
\]

where \( \lambda_{\text{tr}} \) is the transport mean free path for elastic
scattering. Monte Carlo simulations have shown that
the actual attenuation as a function of depth can be
more complicated than described above [105–107].

Values of \( L \) averaged over the energy spectrum of
the emitted electrons are 5–15 Å for metals [108–110]
to hundreds and even thousands of Å for wide band
gap insulators, such as the noble gas solids [111,112].

### 3.3. Transmission through the surface barrier

The surface electrostatic potential is corrugated on
the atomic scale, small compared with the scale of the
wavelength of electrons of a few eV, suggesting that it
is a good approximation to consider the surface as
planar. In fact, photoemission experiments in single
crystals which show that the momentum of the electron
parallel to the surface, \( h k_{\parallel} \), is conserved during emis-

\[
E' = h k_{\parallel} - \mu
\]

\[\mu = \frac{e \phi}{h} - \frac{e V}{h} \]

\[\mu = \frac{e \phi}{h} + \frac{e V}{h} \]

where \( \mu \) is the chemical potential, \( e \) is the charge
of an electron, \( m \) is the mass of the electron, \( V \) is the
potential, \( h \) is Planck's constant, and \( \phi \) is the
work function.

The probability of transmission through the barrier \( T \)
can then be calculated by assuming that all electrons in the
cone with \( \theta' < \theta_{\text{max}} \) can escape. Therefore \( T \)
depends on the shape of the angular distribution of the
electrons reaching the surface. When elastic scattering
can be neglected [103], electrons can be considered to
travel in a straight line to the surface attenuating in number according to \( \exp(-z/L \exp(-2/L)) \). Then

\[
T(E) = \frac{E}{2 E + I}
\]

On the other hand, when elastic scattering is impor-
tant, the transmission through the barrier can be calcu-
lated assuming that electrons arrive at the surface
isotropically in the half space inside the solid. In this
case,

\[
T(E) = \frac{1}{2} \left( 1 - \sqrt{\frac{I}{E + I}} \right)
\]

These escape probabilities are classical. Quantum me-
chanically, not all electrons with the escape condition
can escape. Reflection can occur even if \( E' > I \), when the
uncertainty in the energy of the electron intro-
duced by the finite interaction time \( \tau \) with the surface
is of the order or larger than \( E' \). This uncertainty is
\( \delta E' = h/\tau \), where \( \tau = h/\sigma = \frac{h m}{2E'} \) and \( b \) is
the width of the barrier. This means reflection can occur for
\( h(m/2E')^{1/2} > b \). Thus quantum barrier ef-
ffects will be important for \( E \leq 0.5 \text{ eV} \) for a barrier
width \( b = 2 \text{ Å} \). The quantum mechanical reduction in
the transmission above the barrier is very strong in
thermoionic emission, where electron energies are very
small: it reduces the thermoionic "A-factor," and hence
the emission current, by 25–50\% [114]. Hence, one
should also expect important reductions in KEE near
threshold.

The value of the inner potential \( I \) that influences
electron escape, is found to be of the order of 11–15
eV in metals from LEED measurements [115]. It is
remarkable that these are close to the values expected
from a free-electron model, \( E_F + \phi \), as if band struc-
ture effects were not important. This is possibly related to the short lifetime of excited electrons in metals, which broaden significantly the states in the conduction band. Recent inverse-photoemission experiments [116] have revealed that the width of s and p conduction band states for metals seem to follow a universal curve \( I_s(E') = 0.13(E' - E_p) \), or typically \( \sim 0.5 \text{ eV} \) at the vacuum level. For d-like bands, the widths are even larger, \( \sim 0.6(E' - E_p) \).

As mentioned above, the barrier \( I \) for insulators is the electron affinity \( \chi \), which can be as low as a fraction of an eV or even negative, such as in the (111) face of diamond, in solid Ar or in semiconductors with special surface coatings [117]. This reduced barrier is one of the main reasons for the larger EE yields of insulators as compared with metals.

An interesting case is that of PEE, where the three-step model does not hold in a strict sense. The wave function of the intervening electrons extend over the vacuum level. For d-like bands, the widths are even more pronounced in situations which render large average electron yields [122,123]. In these cases, the ejected electrons will move in the field of the other electrons and their images; their trajectories will be deflected, compared to those of electrons emitted alone. The ejected charge cloud will evolve in time according to the internal fields and the applied external extraction field. Electrons in the front of the charge cloud will receive extra energy while those at the trailing side will be slowed down, even pushed back to the solid (depending on the extraction field), as observed in pulsed-laser induced photoemission [124,125]. The amount of energy that can be gained can be of the order of \( U = \gamma e^2/r_0 \), where \( r_0 \) is the initial radius of the electron cloud \( U \sim 20 \text{ eV} \) for \( r_0 = 15 \text{ Å} \) and \( \gamma = 20 \). Then, this space charge should act to decrease the yields, flatten the angular distribution, broaden the energy distribution of the electrons and affect the I–V characteristics of the target-collector diode. The effects should be sought after particularly in cases where \( \gamma \) is very high. Electron yields in the hundreds have been seen for PEE of very highly charged ions [42]. In KEE from solid Ar, we have observed \( \gamma \) of several thousands [126]; similar values are expected in other materials with negative electron affinity. Even higher yields should be possible using fast heavy ions and conditions of oblique incidence.

Large electron yields also result from energetic ion–surface collisions at grazing incidence. For instance, collisions of 0.5–2 MeV He\(^+\) on SnTe(001) surfaces, produce electron yields larger than 200 for

V. ELECTRON EMISSION
ion incidence of less than 1° to the surface [127]. One should expect even higher yields at lower energies, close to the stopping power maximum. One can visualize that the trajectory of the ion is accompanied by a cloud of ejected electrons (fig. 8). A convoy electron which would normally be ejected along the ion path with a velocity close to that of the ion, would be pushed to higher energies. It is proposed here that this is the case for energy shifts observed [128-132] in convoy EE at grazing incidence which has been attributed to acceleration by the image charge induced by the projectile [133,134].

5. Yields

To calculate differential and total yields one has to develop quantitative descriptions of the mechanisms shown above and assemble them to derive observable quantities. No complete theory exists at this time although some special cases have been derived where simplifications are possible. For instance, at high velocities, one can neglect recoil effects and consider that the projectile does not lose much energy over the escape depth. In this case, the number of primary events is independent of depth \( z \). One then needs energy and angular distributions of these 1G electrons as input to a calculation of the electron transport and multiplication in the cascade. These can be obtained from atomic physics calculations or experiments, and one can use electron gas models for the valence band, which gives the most important contribution at low impact velocities. At high velocities, most inner shells can be excited, each contributing approximately in proportion to its number of electrons, and so it is important to describe well inner-shell excitations and the subsequent Auger decay.

Once the excited electron sources are obtained, calculation of the electron cascade can proceed using transport theory or Monte Carlo simulations starting with electron scattering data from gas-phase collisions or free-electron models, as appropriate to the type of solid. Here the main difficulty is the lack of an adequate description of elastic scattering at the lower electron energies where quantum effects are important. Once the flow of the electrons at the surface is obtained one can calculate the transport through the barrier. In this case, the main difficulty is the estimation of the inner potential and quantum reflection effects.

Calculations at low velocities need to take into account excitations by fast target recoils, which require an evaluation of the atomic cascade. Scattering of the projectile near the surface makes the ionization path longer inside the escape region. If the scattering is very strong, the projectile can backscatter producing additional excitation. The maximum excitation is caused by a projectile which scatters and follows a trajectory parallel to the surface, just below it. This process is unlikely and will not contribute to any significant extent to the total yield. It can, nevertheless, be observed as a finite probability of ejecting a very large number of electrons \( n \) (\( n \gg 1 \)).

A good description of valence excitations by projectiles and recoils becomes more important since inner-shell contributions are small. To calculate the distribution of 1G electrons one has to follow the trajectories of projectile and target atoms (e.g., by using Monte Carlo or molecular dynamics simulations). For each collision one calculates the inelastic energy transfer by using, for instance, Firsov's formula or improved versions [135,136]. If this calculated energy transfer is larger than \( U \), one counts an excited electron from which one builds a distribution of ionization events, \( n(z) \) as a function of distance \( z \) to the surface. At low enough energies, cascade multiplication can be neglected, and one can equate \( n(z) \) to the depth distribution of 1G electrons. If one neglects inelastic electron collisions that do not attenuate the electron flux, one can calculate the energy distribution of ejected electrons from

\[
\frac{dy}{dE} = T(E') \int n(z, E') \exp(-z/L(E')) \, dz,
\]

where \( E = E' - I \), from which one can deduce the total yield by integration.

Another simple case is that of KEE near threshold. When the mass of the projectile is larger than that of the target atoms, the threshold behavior of KEE will be dominated by recoil effects, since the recoils can be faster than the projectile [53]. When the projectiles are
lighter than the target atoms, KEE at threshold is produced by inelastic ion–surface collisions with surface atoms. One can disregard electron transport in first approximation and assume that all electrons in the escape cone (eq. (11)) will go into vacuum. Then the energy distribution of emitted electrons is given by

$$\frac{d\gamma}{dN} = \frac{d\sigma}{dE}NaT(E), \quad (15)$$

where \(\sigma\) is the ionization cross section and \(Na\) is the surface density of target atoms. The use of the stopping power is not justified here because the excitation of electrons above the vacuum level is dominated by rare events rather than by average energy loss collisions [137]. Another important consideration is that the accuracy of the description of the escape function \(T(E')\) is more important at threshold where most of the electrons have very small energy. Integration of eq. (14) and comparison with eq. (1) show the parallelism between gas-phase ionization and EE from gas-covered surfaces first demonstrated by Amme [138].

6. Adsorbed layers and insulators

It has been known for a long time that EE from insulators is larger than from metals or semiconductors. In most of the literature this is attributed to result from a larger mean electron escape depth due to the reduced electron scattering for ejected electron energies lower than the band gap. Another factor, often more important, is that excited electrons escape more easily from insulators due to a reduced surface barrier. The relative importance of these two factors can be discerned by analyzing the effect of the thickness of the insulating layer.

Adsorbed layers already have a very strong influence on electron yields. The lack of specification of the surface for targets exposed to air hinders the possibility to extract information about mechanisms from electron yields. This is true for almost all the work done previously to 1950, but occasionally one finds this shortcoming in current publications. An exception seems to be the case of measurements on carbon foils, where at least good reproducibility is often (but not always) found between different laboratories.

The adsorption of small quantities of gas (of the order of a monolayer or less) can change EE for many reasons. The most important seem to be (1) a different electron excitation probability for the adsorbed species as compared to the bulk, and (2) a change in the surface barrier. The change in the electron attenuation length is a second order effect for the thinner layers. Comparative experiments on the adsorption of oxygen on clean Al and Mo surfaces showed very large effects on the yields [139]. Since one can expect a similar
electronic configuration in the oxygen in both cases, the reason for the large differences in the two materials is not likely to result from (1) above. This is further supported by the observation that the change in the yields is not proportional to the oxygen concentration. The change in the surface barrier appears to be the main factor affecting the yields, but it is not necessarily related to changes in the work function. Adsorbed gas generally (but not always) causes an increase in the electron yields [139]; the relative change in the yields is larger than the lower incident energy [140].

EE from thick insulators is an intriguing problem which is difficult to study due to surface charging. We have recently reported [126] measurements of KEE from thin Ar films. Argon is an interesting material for EE studies because it has a large band gap, an extremely large mean electron escape depth (of the order of a micron), and a negative electron affinity (conduction band above the vacuum level). We have observed nearly complete extraction of electrons from thin films and, under some conditions, dielectric breakdown during and after ion bombardment in the presence of a weak external electric field.

7. Conclusions

Electron emission under ion impact results from direct ionization of the projectile or target atoms plus additional ionizations produced by energetic secondary electrons. The study of EE provides some of the most detailed pictures of inelastic ion–surface collisions, giving insight on mechanisms which can be applied to study other processes, such as energy loss, charge transfer, ionization damage and desorption. These mechanisms can be described conceptually but calculations are still far from the level of accuracy possible, for instance in the emission of atoms (sputtering). Besides the lack of general theories there are still many unsolved problems in the understanding of high ionization densities, excitations by slow projectiles and by molecules or clusters, the threshold behavior of KEE, quantum effects in the motion of excited electrons, final state interactions, and ionization and breakdown in insulators.

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V. ELECTRON EMISSION
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