

FIELD IONIZATION

Electric fields play an important role in understanding the observed physical properties in both laboratory and natural plasmas. Electric fields are not only due to external fields but also to ions and free electrons in the environment of the observed object. We will first discuss the basic definition of field ionization. Electric fields allow the valence electron of an

atom to ionize by tunneling through the combined electric and Coulomb potential. Hence in external electric fields all bound states become quasibound due to tunneling. Then we will discuss tunneling through a potential barrier in general, followed by a basic discussion of the Stark effect. Because not only static external electric fields, which give rise to the celebrated Stark effect, are of principal interest, we will also discuss the behavior of a Rydberg electron under subpicosecond electric pulses. These studies are not only of fundamental interest but give also a better understanding of problems such as the transport of ions and atoms through solids or for fusion plasma modeling and diagnostics. To get a better feeling for the characteristic times involved we will add some remarks about wave-packet propagation due to the coherent excitation of Rydberg states via an initial laser packet. Impurities can be regarded as solid-state atoms. We will also briefly discuss ionized impurities before turning to the fundamental questions of spectral line broadening. Then we will discuss some plasma aspects, like the electron density in some natural plasmas and the distribution among the ionization stages of an atom in the ionization equilibrium.

Ionization is not only due to external electric fields but also to single- or multiphoton ionization. These topics will be the subject of the chapter "Photoionization." Historically important for the development of quantum mechanics was the photoelectric effect, which will be explained later. After that we will discuss the basic definitions of photoionization and selection rules for radiative transitions due to the dipole approximation. If ionization is not possible by absorption of a single photon, ionization could be also achieved by multiphoton absorption. In such processes, not only the least number of photons necessary for ionization will be absorbed by the valence electron. The absorption of photons in excess gives rise to the above-threshold ionization, as discussed later. This article will be completed by a discussion of impact ionization, which is due to the collision of an atom or ion with charged particles.

FIELD IONIZATION

Basic Definition

The motion of an atomic electron in an external electric field is subject to two fields of force: an attractive Coulomb force due to the positive atomic core and the applied external electric field. Hence the potential energy of the electron is given by

$$V_t(\mathbf{r}) = -\frac{Zq^2}{|\mathbf{r}|} + qFz, \mathbf{r} = (x, y, z) \quad (1)$$

if the electric field axis points into the z direction and the electric field strength is measured in atomic units, that is, in units of $F_0 = 5.14 \times 10^9$ V/cm. An example is shown in Fig. 1.

The total potential V_t has a saddle point for $x = 0 = y$, $z = \sqrt{q/F}$ and here the potential energy takes the value $V_s = -2q\sqrt{ZqF}$. Moreover, for $Z = 1$ the contribution to the potential energy of the two fields is identical (see Fig. 1). A classical electron will be bound for energies smaller the saddle-point energy V_s inside the potential walls as the walls are impenetrable barriers. As suggested first in 1928 by Oppenheimer (1) the application of electric fields enables bound electrons to escape by tunneling in a process called field ionization.

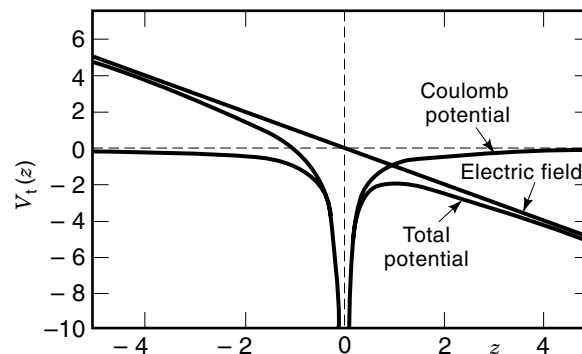


Figure 1. Effect of the electric field on the potential energy of an electron in the Coulomb field of a proton in atomic units. (The electric field strength is 5.14×10^9 V/cm).

Potential Barrier

One of the most fascinating quantum phenomena is tunneling. A classical particle with energy E smaller than the potential height V of a potential barrier cannot penetrate this wall. In quantum mechanics the continuity of the wave function in space implies that the amplitude of a wave function will only decrease inside the wall and hence there is a finite probability of finding the particle beyond the classical turning point. Therefore a quantum particle has a finite probability to penetrate any potential barrier, and thus tunneling phenomena are strictly quantum mechanical with no counterpart in classical dynamics.

For the potential wall, Fig. 2, the transmission coefficient or probability for tunneling is $P_t \propto \exp[(2d/\hbar)\sqrt{2m(V-E)}]$, where \hbar is the Planck's constant, d is the width and V is the height of the potential wall, and E is the energy of the particle. For an electron, for example, the probability P_t is ≈ 0.1 for tunneling through a barrier of width $d = 0.2$ nm and $V - E \approx 1$ eV. In nature there are numerous examples for tunneling, for example, field ionization, nuclear fusion and fission, impurity tunneling, and so forth, which give rise to many applications, for example, tunneling microscopes (2), tunnel and Esaki diodes (3), and Josephson junctions. Details about tunneling can be found in any quantum-mechanics textbook, for example, in Cohen-Tannoudji, Diu, and Laloë (4).

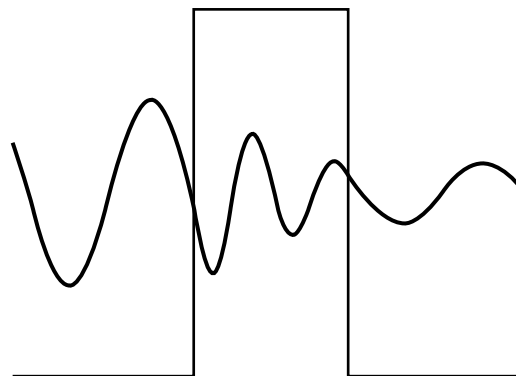


Figure 2. Potential barrier; the energy is such that a classical particle would be totally reflected by the barrier. On the left-hand side: The superposition of the incoming and the reflected wave and on the right-hand side of the barrier the outgoing wave.

As tunneling phenomena are strictly quantum mechanical the tunneling process is described by the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t) \quad (2)$$

where $V(\mathbf{r})$ is the potential, Δ is the Laplacian operator, \mathbf{r} is the coordinates, t is the time, $\hbar = h/2\pi$, and m is the mass of the particle. During the tunneling process the particle is behaving like a wave but can be detected in the region beyond the barrier as a localized particle. Because the wave function is a continuous function the stationary wave function $\phi(\mathbf{r})$ can be computed by matching the solution in different areas together:

$$\phi_{\text{out}}(\mathbf{r}_s) = \phi_{\text{in}}(\mathbf{r}_s) \quad (3)$$

$$\nabla\phi_{\text{out}}(\mathbf{r}_s) = \nabla\phi_{\text{in}}(\mathbf{r}_s) \quad (4)$$

with ϕ_{in} and ϕ_{out} the solutions in- and outside the barrier and \mathbf{r}_s the border position of the barrier. In the WKB approximation the tunneling probability P_t for one-dimensional systems is proportional to

$$P_t \propto \exp\left[-2\int_a^b\left(\frac{2m}{\hbar^2}[V(r)-E]\right)dr\right] \quad (5)$$

where a and b correspond to the classical turning points, and the proportionality prefactor depends on whether the potential changes continuously or not. If the potential changes continuously at both turning points this prefactor is 1, and for a discontinuity it becomes energy dependent. Solutions for wave packets can be obtained by Fourier-transforming the stationary solution. In this context the question arises: Is there a time analog to the classical time for a particle tunneling through a potential barrier? This is a current controversy under discussion (5) because some experimental results show superluminal velocities (6). A critical review can be found, for example, in Refs. 7 and 8.

The Stark Effect

Figure 1 shows the effect of an electric field on the total potential of an electron in the Coulomb field of a positive charge. Due to tunneling there is even for energies smaller the saddle-point potential V_s a nonzero probability of the electron to penetrate through the potential barrier. Thus the classically bound region is always coupled to the dynamical unbound region. As the tunneling probability depends on both the height and the width of the barrier, the effect of field ionization becomes most important close to the saddle-point energy.

In general, the effect of a static electric field on atomic spectra is called Stark effect. The corresponding behavior for an external magnetic field is termed the Zeeman effect. A collection of recent articles that present the state of the art in the theoretical, computational, and experimental studies of atoms, molecules, and quantum nanostructures in strong external fields can be found in Schmelcher and Schweizer (9).

For sufficiently small electric fields the electric field potential can be treated as a perturbation of the Coulomb potential. The first-order corrections to the energy are called the linear Stark effect. As the electric field potential is proportional to

the distance from the atomic center the linear Stark effect vanishes if the unperturbed eigenstates of the physical system under consideration are not degenerate. Due to the symmetries of hydrogenlike atoms the eigenstates are degenerate with respect to the angular momentum and the magnetic quantum number. Therefore the linear Stark effect can be observed only for those atoms and ions. For nonhydrogenic atoms, for example, alkali-metal atoms, the angular momentum degeneracy is removed due to the multielectron interaction of the atomic core and hence only the quadratic Stark effect can be observed. For stronger electric fields perturbation methods are no longer applicable and hence more advanced numerical methods have to be used to obtain the correct spectrum. One of the most challenging numerical methods is given by using complex coordinate rotations of the space coordinates in combination with computations of the Hamiltonian matrix. By this method resonances are mapped onto bound states in a complex extension of the state space. In this context the question arises for which electric field strengths perturbation methods are no longer applicable. A rough estimate is given by the atomic electric field strength, for which the electric field potential equals the Coulomb potential. This field strength depends on the atomic system and on the principal quantum number of the excited state under consideration. For the hydrogen ground state this value is given by the previously mentioned "atomic units" and is equal $F_0 = 5.14 \times 10^9$ V/cm and scales with n^4 , n being the principal quantum number. Therefore for the $n = 500$ excited states the critical value is already 82 mV/cm.

The Hamiltonian of a hydrogenlike atom placed in an homogeneous static electric field directed along the z axis reads in atomic units

$$V(\mathbf{r}) = -\frac{1}{r} + Fz \quad (6)$$

and hence the Schrödinger equation becomes separable in parabolic coordinates

$$\zeta = r+z, \quad \eta = r-z \quad (7)$$

The resulting equations for ζ and η are

$$\left(\frac{d^2}{d\zeta^2} - \frac{m^2-1}{4\zeta^2} + \frac{\beta}{\zeta} - \frac{F}{4}\zeta + \frac{E}{2}\right)f(\zeta) = 0 \quad (8)$$

$$\left(\frac{d^2}{d\eta^2} - \frac{m^2-1}{4\eta^2} + \frac{1-\beta}{\eta} + \frac{F}{4}\eta + \frac{E}{2}\right)g(\eta) = 0 \quad (9)$$

with E the energy, m the conserved magnetic quantum number, and β the separation constant, the so-called fractional charge. The uphill equation (8) has only bound solutions, whereas the downhill equation (9) describes the tunneling solution. The eigenstates f and g are characterized by the parabolic quantum numbers n_1 and n_2 , which are related to the principal quantum number n via

$$n = n_1 + n_2 + |m| + 1 \quad (10)$$

and parabolic quantum states are usually represented by $|nkm\rangle$, with $k = n_1 - n_2$. The fractional charge is given by

$2\beta - 1 = (n_1 - n_2)/n$ and the energy eigenvalue in first-order perturbation theory by

$$E = -\frac{1}{2n^2} + \frac{3nkF}{2} \quad (11)$$

In the field-free atom the n -manifold is degenerate and, neglecting the electron spin, consists of n^2 states corresponding to different values for the angular momentum l and the magnetic quantum number m . This degeneracy is broken by the electric field. To describe the Stark effect in Rydberg spectra of bound and autoionizing states Harmin (10) has developed a quantum defect model in which the Stark effect is only taken into account for large distances from the atomic core. All states are quasibound since they can tunnel through the potential barrier into the continuum and hence the eigenenergies are associated with a complex energy value the real part of which E_r , gives the energy and the imaginary part the half-width, $-\Gamma/2$, of the decaying state. For time-independent quantum systems the time development of a state is given by $|\mathbf{r}, t\rangle = \exp(-iEt/\hbar)|\mathbf{r}\rangle$ with $E = E_r - \Gamma/2$ and hence Γ is the transition rate given by Fermi's golden rule (4). The complex energies can be directly obtained by the complex coordinate rotation (11).

$$\mathbf{r} \rightarrow \mathbf{r} \exp(i\Theta) \quad (12)$$

As shown by Seipp, Taylor, and Schweizer (12) tunneling below the classical ionization limit E_{sp} is relatively weak and even above E_{sp} some resonances exist with negligible small widths. Qualitative differences occur for hydrogen and alkali-metal atoms due to the separability of hydrogen in electric fields. The spectra for alkali-metal atoms are much more disordered and no closely bound resonances above the classical ionization limit occur. If we turn on a magnetic field parallel to the electric field all resonances get shifted in the direction of positive energy, as is expected from the positive quadratic Zeeman effect. For more details see Ref. 9. Strong electric and magnetic fields are not only of interest under laboratory conditions but also in quest of observed optical absorption structures of compact astronomical objects. For example, for magnetic white dwarf stars additional electric fields (13) of the order of 10^8 V/cm occur, which give rise to an observable shift of the spectral lines.

Stark effects are not only due to external electric fields. Atomic beams with the beam direction not in coincidence with the magnetic field axis of an external magnetic field give rise to the so-called motional Stark effect. In external magnetic fields the center-of-mass coordinate is no longer separable from the relative coordinate and hence in the Schrödinger equation of the relative coordinates an additional potential-like term occurs, which depends linearly on the relative coordinates and on the wedge product of the magnetic field with the center-of-mass momentum. Therefore this additional term shows the same effect as an external electric field and is therefore called motional electric field.

Studying the external fields for the hydrogen atom gives also some information about shallow donor states, as the Hamiltonian for many systems are equivalent. For example, for the donor in GaAs the effective electron mass is 0.0665, and the dielectric constant 12.56. In atomic units these two values are equal to 1. The Rydberg constant becomes 46.1

(11×10^4) and the Bohr radius 9.96 nm (0.0529 nm), where the values in parentheses are the corresponding hydrogen values. Hence an electric field of about 10^{10} V/m will have the same impact on a H atom as a field of 2×10^4 V/m on a donor. More details can be found, e.g., in Refs. 14 and 15.

Pulsed Field Ionization

Recently various experimental and numerical methods for investigating the dynamics of Rydberg electrons in external fields have been developed. The Rydberg wave packets have been created by photoexcitation of ground-state atoms using ultrashort laser pulses. The bandwidth of these laser pulses exceed the level spacing in the Rydberg-energy region. Therefore the Rydberg wave packet is built by several dipole-allowed coherently excited Rydberg levels. Time-resolved spectroscopic experiments show radial and angular oscillations of the electronic Rydberg wave packet. The period of the radial oscillation of the Rydberg wave packet is given by the Kepler time

$$\tau_{\text{rad}} = 2\pi \left(\frac{1}{-2E} \right)^{-3/2} \quad (13)$$

with E the energy expectation value. Typical Kepler times are of the order of 2 ps. The static external electric field produces a torque that causes the angular momentum to progress from its initial value towards higher angular moments. The angular return time depends on the electric field strength and is given to first order by

$$\tau_{\text{ang}} = \frac{2\pi}{3} \left(\frac{1}{-2E} \right)^{3/2} F \quad (14)$$

this yields typically values of 10 to 50 ps for electric field strengths of 200 V/cm to 900 V/cm; see Ref. 16 and references therein.

Very recently, experimental (17) and theoretical (18) work has explored the evolution of Rydberg wave packets of alkali-metal atoms subject to subpicosecond "half-cycle" electromagnetic pulses. The characteristics of half-cycle pulses are very similar to electric field pulses generated by the passing-by projectile in an ion-atom collision. Thus the study of the dynamics of Rydberg atoms subject to those pulses is in addition of practical importance in problems such as transport of ions and atoms through solids or plasma modeling and diagnostics of high-temperature plasmas, like fusion plasma.

In contrast to the laser-excited wave packets the bandwidth of the initial laser wave packet is so small, that only a single stationary state will be populated. This Rydberg alkali-metal state will then be subject to a kick from a unidirectional, pulsed electric field. The pulses in this experiment are short compared to the Kepler period of the Rydberg electron. Approximately the only effect of this impulse is to change the electron's momentum in the field direction. If the electric field points into the z direction the electron's change of energy is given by

$$\Delta E = \Delta p p_z + \Delta p^2/2 \quad (15)$$

where Δp is the change of the momentum of the electron in the field direction. If this change in the energy is greater than the binding energy $E_B = -\frac{1}{2}(n - \delta_l)^2$, with n the principal

quantum number and δ_i the quantum defect of the alkali-metal atom, the electron will leave the atom. Therefore the percentage of the atoms ionized equals the percentage of the electrons with the z component of the electrons larger than

$$p_z \geq \frac{-2E_B - \Delta p^2}{2\Delta p} \quad (16)$$

Note, that in a dc electric field the energy levels are energetically split due to the Stark effect and all states become quasisubbound due to the finite tunneling probability in an electric field, whereas due to the short electric pulse in pulsed field ionization tunneling becomes unimportant. Ionization in pulsed electric fields are only due to the momentum change of the Rydberg electron due to the electric field kick. This interpretation is supported by both the experimental results and the theoretical computations. Therefore the quantum dynamics is adequately described by a single electron in the combined field of the effective one-electron atomic Hamiltonian and pulsed electric field. For more details see Ref. 18 and references therein.

Ionized Impurities

Real crystals are imperfect and contain a variety of types of defects. Defects at the atomic level are point defects. Point defects can be native defects, such as vacancies and interstitials of the crystal atoms, as well as foreign—impurity—atoms, which are generally intentionally added to the material. Impurities give rise to two kinds of energy levels, which are often denoted as shallow and deep energy levels. Deep energy levels are levels towards the middle of the energy gap, whereas shallow impurities have levels close to the band gap. Shallow impurities are classified as donors or acceptors depending on whether they produce electron or hole conductivity. An impurity breaks the crystal symmetry of a perfect crystal and will give rise to different electric properties.

In a simple picture but with sufficient accuracy shallow donor states can often be described by a solid-state analog (previously noted) of the hydrogen atom with rescaled energy, Bohr radius, effective charge, and mass (19). Under this assumption, the donor electron will have hydrogenlike bound states with energy

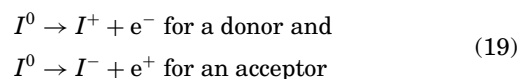
$$E_n = \frac{-\mathcal{R}}{2n^2} \quad (17)$$

but with a Rydberg constant \mathcal{R} much smaller and will to some extent show the same qualitative spectroscopic behavior under external fields as the hydrogen atom. Note that since the system is in a medium the Coulomb potential have to be changed to

$$\frac{e}{r} \rightarrow \frac{e}{\epsilon r} \quad (18)$$

where ϵ is the dielectric constant of the material.

We will now consider the ionization of a neutral impurity in a graphical way:



with I^0 the neutral impurity. The donor ionization reaction corresponds to an emission of an electron to the conduction band and the acceptor ionization reaction to an emission of a hole to the valence band, which is equivalently described by the capture of an electron from the valence band. These processes could also be generalized to multi-ionized donors and acceptors. The single ionization energy is 10^{-4} to 10^{-2} times smaller the hydrogen ionization energy of 13.6 eV. Therefore at room temperature most impurities are ionized and contribute to the conductivity because their ionization energies are comparable to $k_B T$, k_B being the Boltzmann constant. (1 eV is equivalent to a temperature of 11,400 K. Hence for hydrogen the ionization energy is equivalent to about 150,000 K, whereas for the previously mentioned shallow donor state of GaAs we get about 65 K.) Therefore even at low temperatures a finite nonzero concentration of ionized impurities exist. These ionized impurities create electric fields due to their charge and hence neutral donors are embedded in local electric fields with a randomly distributed field strength, and this causes Stark shifting in the level structure. Because in electric fields the angular momentum is no longer conserved, donor states with different quantum numbers are mixed and forbidden transitions (discussed later) are observed. Moreover, this leads to an inhomogeneous line broadening (14). For more details see, for example, Refs. 20 and 21.

Spectral Line Broadening

Any observed spectral line shape has a finite width not only due to the instrument used in the creation and observation process but due to fundamental processes. In general we distinguish between three different sources of these broadening processes: the natural broadening, the Doppler broadening, and the pressure broadening.

The natural broadening of spectral lines is due to the finite lifetime of the corresponding states. Due to the uncertainty principle $\Delta E \Delta t \approx \hbar$, the energy spread of a transition is inversely proportional to its life time. In the optical region the natural broadening is of the order of 10^{-7} to 10^{-8} of the frequency of the observed line. Classically this can be also understood by the damping of an harmonic oscillation.

Doppler broadening is due to the Doppler effect, which is the shift in the wavelength caused by the relative velocity between the atom (source) and the observer. In astrophysics the so-called redshift of atomic spectral lines is used to measure the velocity of far stars compared to our earth and estimating from this value the distance of the observed star. In addition, for extremely compact astronomical objects the gravitational redshift, due to the strong gravitational potential of massive stars, could be observed.

Atoms, ions, or molecules are never isolated single objects. This gives rise to effects due to neighboring objects, which is called pressure broadening. An emitting atom within a certain distance of a neighboring ion or electron is perturbed by an electric field, and the interaction between the atom and the field is described by the Stark effect. The electric field due to plasma ions and electrons near the radiating object is called the plasma microfield. A fundamental role in the microfield theory is played by the Holtsmark model, which approximates the effect of neighboring charged particles by an aggregate of randomly disposed immobile ions and electrons. Hence it is obvious that the width of the spectral lines depend on

the temperature, pressure, and electron density of the environment of the radiating object. For more details, see Ref. 22.

Plasma Aspects

Plasma, generally speaking, is an internal electric neutral gas that consists of neutral and ionized atoms and molecules and of electrons due to the ionization processes. Typical temperatures of plasmas are above 10,000 K, in which the fastest particles in the thermal Maxwell distribution undergo collisions energetic enough for ionization processes.

Plasma can also exist under much lower temperatures. In the vacuum of outer space ionization of hydrogen in hydrogen clouds is due to photoionization by starlight. The density in these clouds is extremely small and hence collisions are rare. Consequently nearly all matter in the universe is in the plasma state. On earth, however, the atmospheric density cannot support such plasma. Nevertheless plasma can also exist at room temperature in metals and semiconductors due to the extremely small band energies.

One of the basic characteristics of plasmas is the importance of collective effects. Every charged particle interacts with several neighbors because of the long-range electrostatic forces. Hence the motion of the plasma particles are correlated. One important criterion is the Debye shielding radius, which measures the distance to which the electric fields of an individual charged particle extends before it is effectively shielded by its opposite charged neighbors. One of the fundamental plasma parameters is the electron density. In simple models the Debye shielding radius as well as the Holtsmark electric field is given by the electron density. For the interstellar matter the electron density varies from parts up to a few tens electrons per cm^{-3} , for gaseous nebula this is of the order of a few hundred cm^{-3} , in the solar corona 10^4 cm^{-3} , for flames of the order of 10^8 cm^{-3} and in the stellar atmospheres it is up to roughly 10^{18} cm^{-3} (see Ref. 23).

The Maxwell relation describes the distribution of the velocity among particles and the Boltzmann relation the distribution of the population of the discrete energy levels. The distribution among the ionization stages of an atom in the ionization equilibrium due to the process



is described by Saha's equation (23):

$$\frac{N_e N_i^{(n+1)}}{N_j^{(n)}} = \frac{2(2\pi m k_B T)^{3/2} g_i^{(n+1)}}{h^3 g_j^{(n)}} \exp\left(\frac{\kappa + E_i - E_j}{k_B T}\right) \quad (21)$$

where N_e is the number density for the electron, $N_k^{(x)}$ is the x -times ionized atom in the k th excited state, g are the corresponding weights due to the degeneracy of the state under consideration, E_0 is the corresponding energies, κ is the ionization energy, m is the electron mass, T is the temperature, and k_B is the Boltzmann constant, and h is the Planck constant. Thus by measuring the absolute spectral intensities the particle density in a certain excited state can be obtained and hence the plasma densities. All the different thermodynamical processes—radiation, kinetic distribution of the particle, distribution of the atomic excitation and ionization stage—described by the Planck, Maxwell, Boltzmann, and Saha

equation involve absolute temperatures. If all these temperatures are equal the plasma is in the local thermodynamical equilibrium, which is usually assumed to compute from spectral data the plasma densities and single ion densities. Because of these additional limitations the overall accuracy is often poor. (For more details see Ref. 24.)

PHOTOIONIZATION

The Photoelectric Effect and Ionization Potential

The emission of electrons from the surface of a metal was discovered by Hertz in 1887. Later experiments by Lenard showed that the kinetic energy of the emitted electron was independent of the intensity of the incident light and that there was no emission unless the frequency of the light was greater than a threshold value typical of each element. Einstein realized that this is what is to be expected on the hypothesis that light is absorbed in quanta of amount $\hbar\omega$. In the photoelectric effect an electron at the surface of the metal gains an energy $\hbar\omega$ by the absorption of a photon. The maximum kinetic energy of the ejected electron is

$$\frac{1}{2}mv_{\max}^2 = \hbar\omega - e\Phi \quad (22)$$

where Φ is the contact potential or the work function of the surface measured in electron volts (see Table 1). Einstein's theory predicts that the maximum kinetic energy of the emitted photoelectron is a linear function of the frequency of the incident light, a result which was later confirmed experimentally by Millikan (1916) and which allowed to measure the value of the Planck constant h .

The lowest level is called the ground state; higher levels are called excited states. The least energy E needed to remove a single electron from an atom or ion in its ground state is called the ionization energy of the atom or ion. This energy corresponds to a potential difference—the ionization potential—for a bound electron being removed to infinity. This ionization could be due to particle scattering (impact ionization) or due to photoionization.

Photoionization

Although investigations of photoionization started already at the end of the nineteenth century when the photoelectric effect was discovered, photoionization still remains an active field in research that got an additional stimulus from laser physics during the last two decades.

In the following we will describe some photorelated processes in a graphical way. In this process descriptions A is either an atom, or ion, or molecule but could also stand, e.g., for a metal cluster. A^* is the excited object, A^+ is the same

Table 1. Contact Potential Φ and Corresponding Wavelength of the Incident Light, the So-Called Red Border Wavelength λ_r .

	λ_r (Å)	Φ (eV)		λ_r (Å)	Φ (eV)
Li	5280	2.38	Cu	2880	4.29
Na	5300	2.33	Ag	2610	4.73
K	5460	2.26	Au	2600	4.76
Rb	5800	2.13	Pt	1960	6.37
Cs	6400	1.93	W	2720	4.57

object but one-time-higher ionized than A . Therefore if A stands, e.g., for the three-times ionized nitrogen N IV, A^+ is one times-higher-ionized, hence in the example N V. (In this notation the Roman numerals stands for the ionization stage, I for neutral, II for single ionized, III for double ionized objects, and so forth.) Graphically the excitation of an object A can be described via



In this photoabsorption process the photon $h\nu$ is annihilated. When $h\nu$ exceeds the ionization energy of A , the process of photoionization can occur:



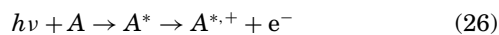
The inverse process is known as radiative recombination.

The photoionization reaction



involving a negative ion (excited or not) A^- is called photodetachment.

Photoionization cross sections are dominated by resonances in certain energy regions. In this energy area not only direct photoionization process, like the one described by Eq. (24), are of importance, but in addition ionization processes via an intermediate resonance state



The interference between the direct and the intermediate photoionization process leads to the so-called Fano line profile in the photoionization cross section $\sigma(E)$, which can be parameterized by a simple formula

$$\sigma(E) \propto \frac{q + \epsilon}{1 + \epsilon^2} \quad (27)$$

with $\epsilon = (E - E_r)/(\Gamma/2)$, E_r the resonance energy, Γ the resonance width and q the shape parameter.

In all the processes previously described the energy is conserved; hence in the nonrelativistic limit

$$h\nu + W_i = W_f + \frac{\hbar^2 k^2}{2m} \quad (28)$$

where W_i and W_f the eigenenergies of the target in the initial and final state, $h\nu$ the energy of the photons, and the photoelectrons are emitted with momentum k . The ionization cross section is given by the coupling between the target and the electromagnetic field, described by the vector potential \mathbf{A} in the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$. Using Fermi's golden rule in the dipole approximation (4) the transition probability for a transition $|\psi_i\rangle \rightarrow |\psi_f\rangle$ is given by

$$w_{if}^{(q)} = \frac{4}{3} \frac{e^2}{4\pi\epsilon_0} \frac{1}{\hbar} \left(\frac{E_i - E_f}{\hbar c} \right)^3 a_0^2 d_{if}^{(q)} \quad (29)$$

with the dipole strength $d_{if}^{(q)} = |\langle f | r^{(q)} / a_0 | i \rangle|^2$, and $r^{(q)}$ ($q = 0, \pm 1$) the spherical component of the relative vector, E_i and E_f the initial and final energy. Only for hydrogenic atoms and ions transition probabilities can be calculated analytically (25).

For atoms with two and more electrons several approximations have been developed, see, e.g., Bartschat (26) for the R -matrix approach and Fano and Rau (27) for multichannel quantum defect theory, to name only two very successful methods that have also been used in various combinations. The basic idea of the R -matrix approach is to separate the full space into subspaces in which solutions can be numerically obtained and to merge these subsolutions together to get the correct solution; the idea of quantum defects is to describe the deviations from an exact Coulomb potential in the asymptotic limit. Simplified, this leads to a linear combination of the regular and irregular Coulomb function in which the relative contribution of the irregular Coulomb function is weighted by the tangent of the quantum defect.

For radiative transitions, whether photoabsorption, photoemission, or photoionization, several selection rules hold. The interaction with the electromagnetic wave can be expanded as a series in order of decreasing strength: electric dipole, magnetic dipole, electric quadrupole, and so forth. Most computations are done in the electric dipole approximation. This is justified as the dipole transitions are the most probable and hence all other transitions are called *forbidden*. The selection rules are due to the angular momentum coupling of the initial state with the electromagnetic wave in the dipole approximation. The dipole operator is a spherical vector operator; hence we have to couple in the orbit momentum frame the angular momentum l with the angular momentum l' of the initial state. Therefore radiative transitions between states l, m and l', m' are possible only if

$$\Delta l = l' - l = \pm 1, \quad \Delta m = m' - m = 0, \pm 1 \quad (30)$$

hold or in the $j = l \oplus s$ coupling scheme, with l the orbit angular momentum and s the spin

$$\Delta j = 0, \pm 1 \quad \text{but} \quad j = 0 \rightarrow j' = 0 \text{ is forbidden} \quad (31)$$

Insofar as l and s are good quantum numbers, there are additional selection rules

$$\Delta l = 0, \pm 1 \quad \text{but} \quad l = 0 \rightarrow l' = 0 \text{ is forbidden and } \Delta s = 0 \quad (32)$$

(For details about angular momentum coupling see Ref. 4 and about selection rules see Ref. 25). Of course in external electric or magnetic fields additional transitions occur due to inter- l - or inter- m mixing (9), which means that either l or m or both quantum numbers are no longer conserved quantum numbers. This has an important effect, e.g., in the interpretation of observed absorption spectra from magnetic white dwarf stars (13) or the broadening and occurrence of forbidden transitions in shallow donor states (14).

Above-Threshold Ionization

If the energy of a photon is smaller than the ionization potential of the atom in its initial state, ionization will only be possible by absorption of several photons. This process is called multiphoton ionization. Experiments showed that the energy of the emitted electron was larger than the total energy of the least number of photons necessary for ionization. The explanation for this unexpected behavior is that the already emitted electron absorbs additional photons and hence gains a larger kinetic energy. This process is called above threshold

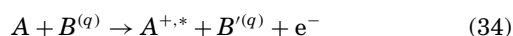
ionization or sometimes excess photon ionization. Hence the kinetic energy of the electron is given by

$$\frac{1}{2}mv_{\max}^2 = n\hbar\omega - e\Phi \quad (33)$$

with n the number of absorbed photons and Φ the ionization potential of the atom and the sufficient number of photons for ionization is smaller than n . The probability for photon absorption in excess by the electron increases with increasing laser intensity and becomes for high laser intensities larger than the probability to absorb only the least of photons necessary for ionization (for further details see Ref. 28).

Impact Ionization

Ionization processes caused by the interaction with charged particles, like electrons, positrons, protons, or even ions, is called impact ionization. These collisions are of importance, for example, in plasma- and astrophysics. In a simplified model this ionization is solely caused by the Coulomb interaction between the charged projectile and the atomic or ion target. In a graphical description these processes can be described by

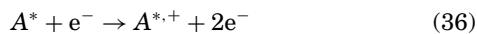


with A the target atom or ion, B the projectile of charge q , $A^{+,*}$ the higher ionized and, in general, excited target object after the scattering process, $B'^{(q)}$ is the projectile after the scattering process and e^- the additional free electron due to the impact-ionization process.

The most important impact-ionization processes are those caused by free electrons and hence are called electron-impact ionization. The following scattering processes are of fundamental importance: The electron-atom collision



in which the energy of the projectile electron is too small to ionize the probably initially excited target atom, direct processes



in which the energy of the projectile electron is sufficiently high to ionize (single ionization or even multi-ionization) the target atom. In addition there are processes with an intermediate resonance state and of course the excited atom could emit photons. Note that due to the selection rules of radiative transition in some cases multiphoton emissions occur. For further details see Ref. 26.

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