Physics of Earth and Space Environments

Vladimir Bychkov
Gennady Golubkov
Anatoly Nikitin *Editors*

The Atmosphere and Ionosphere

Elementary Processes, Discharges and Plasmoids

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The Atmosphere and Ionosphere

Physics of Earth and Space Environments

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Elementary Processes, Discharges and Plasmoids

With 115 Figures and 11 Tables

Springer

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Introduction

In Zelenogradsk, a cozy resort on the coast of the Baltic Sea near Kaliningrad (Russia) city, the 2nd International Conference, “Atmosphere, Ionosphere, Safety” (AIS-2010) took place from June 21 until June 27, 2010. The conference was organized by the State Russian University of I. Kant Institute, Semenov Chemical Physics Institute of the Russian Academy of Sciences and the Pushkov Institute of Terrestrial Magnetism and Radio-waves Propagation of the Russian Academy of Sciences. Financial support was provided by the Russian Fund of Basic Researches, the Presidium of the Russian Academy of Sciences, and the European Office of Aerospace Research & Development (EOARD). Scientists who participated in the conference work were from Russia, Belarus, Ukraine, the United States, Germany, Great Britain, the Netherlands, Belgium, Switzerland, and Japan. During the conference, 12 plenary and more than 60 section reports were delivered, and about 30 posters were presented.

The analysis of reactions in the “atmosphere–ionosphere” system, taking into account the influence of natural and anthropogenic processes, was the central question presented for discussion by the conference participants. Basic attention was given to studying the reasons and cases of the various geophysical and atmospheric phenomena, an estimation of their influence on the biosphere of the Earth and its technological systems, and to development of monitoring systems and decrease in risk of the negative influence of natural processes on mankind’s ability to live. These problems are of interest for a wide range of experts working in various areas of science and technology.

The ionosphere of the Earth is subject to powerful natural influences. Its lower part is disturbed by earthquakes, volcanic eruptions, typhoons, and thunderstorms. From above it is influenced by a set of processes essential for geomagnetic storms. As a result of these processes, such influencing factors as powerful atmospheric disturbances, electric currents, electromagnetic disturbances in various spectral ranges, plasma and optical disturbances, accelerated particles, raised levels of radioactivity, and changed ionic and molecular composition are formed. Moreover, the microwave radiation of highly excited ionosphere particles, accompanying increases of solar activity and occurrences of magnetic storms, has a negative influence on the biosphere of the Earth.

Knowledge of the influencing factors of nature allows us to use them as catastrophic process indicators and to create corresponding monitoring systems on this basis. Thus, there is a requirement to undertake additional research, which necessity is defined by the considerable strengthening of people's ability to live in an ionosphere, leading to the occurrence of new risks. Such are connected with the active development of manned and unmanned orbital systems, and aviation (including the middle atmosphere height), using new kinds of communication.

The Conference's work was carried out in the following directions.

Elementary Processes in the Upper Atmosphere and Ionosphere

During this section, the possibilities of laser control by one of the major atmospheric processes, that is, the dissociative recombination reaction of slow electrons and molecular ions of oxygen, which under certain conditions can be accelerated (or slowed down) by two to three orders of magnitude under the influence of an external field, have been analyzed.

Features of the nonequilibrium microwave radiation spectrum of the upper atmosphere disturbed by electron beams thrown out of the ionosphere during solar activity were discussed.

A report devoted to consideration of the mechanisms of collision and radiating quenching of Rydberg atoms and molecules populating the F-, T-, and D-layers of the upper atmosphere under the influence of these electrons was heard.

The analysis of basic elementary processes proceeding in the lower atmosphere (electron collision ionization of molecule bombardment, electron dissociative attachment, etc.) considered taking into account the influence of atmospheric electricity, and prebreakdown fields.

Explanation of the nature of luminescent layers in the stratosphere ("elfs" and "sprites") during thunderstorm activity that were observed from the satellites "Tatyana-1" and "Tatyana-2", moving at a height of about 850 km, was discussed.

A method of electron wave functions of the system "Rydberg atom + a neutral particle of the environment" was presented. Mechanisms and methods of collision and radiating quenching of the Rydberg atoms process calculations in the upper atmosphere were considered.

Ionosphere Dynamics and Atmosphere–Ionosphere Coupling

The subjects of these reports concerned actual problems of experimental and theoretical research on the ionosphere and the upper atmosphere. Discussion included existing theoretical models of the upper atmosphere and the ionosphere for application possibilities, in particular, the UAM (upper atmosphere model) for interpretation of the results of experimental research, and also the direction of perfection of theoretical approaches. Much attention was given to a discussion of electrodynamic mechanisms of local ionosphere precursors of earthquake formation and the concept of "global electric circuit."

Also, the results of joint research of MSTU (Russia) and GRCG (Germany) on the analysis of wind satellite measurements in the high-altitude thermosphere with the application of a theoretical model of the upper atmosphere (UAM) were presented. Analysis has shown, in both satellite observations and theoretical calculations, that the basic influence on the morphology and dynamics of thermosphere circulation in high latitudes is the impact of the solar wind.

A discussion of results of planetary distribution of the total electron content (TEC) in the atmosphere studied during geomagnetic disturbances and after their termination was presented. It appears that for an explanation of the observable ionosphere dynamics during such periods it is necessary to involve ionospheric physicists in a new class of planetary wave processes, – Poincare's waves.

A new mechanism of a phase delay of satellite signals during the periods of strong geomagnetic disturbances that is caused by the cascade of re-radiations at the Rydberg states of atoms and molecules in the decimeter range, excited by streams of ionosphere electrons, was discussed.

Considerable space in this section's work was given to discussion of theoretical models of different ionosphere areas: the three-dimensional model of "a polar wind," realized with the help of the supercomputer Kant RSU. Also, a one-dimensional model of the ionosphere taking into account a complex set of the photochemical processes developing in the D-area of the ionosphere was considered.

Modeling description of the process of internal gravitational wave propagation from the troposphere to the upper atmosphere was presented. Such research is important to understand the physical mechanisms of the influence of the lower atmosphere on the upper atmosphere and the ionosphere. The results obtained show the possibility of fast (within several minutes) penetration of such waves to the heights of the thermosphere and the influence of this process on upper atmosphere dynamics.

A model of tropical hurricanes, allowing defining the important physical characteristics—the time of the origin and duration of the hurricane, and also its speed of movement—was described. The knowledge of such parameters will allow investigating the influence of large-scale meteorological processes on the dynamics of the upper atmosphere and the ionosphere.

Results of modeling research on the mechanisms of the ionosphere precursors of earthquakes executed within the limits of the theoretical model GSM TIP were discussed. The most effective mechanisms of influence of local disturbances over the earthquake epicenter on parameters of the ionosphere plasmas have been considered, and the conclusion is drawn that the most probable reasons for the occurrence of ionosphere precursors are the disturbance of electric field vertical components and the propagation of short-period internal gravitational waves generated over the epicenter.

The problem of the excited particles, or "hot oxygen" formation, observed in the upper atmosphere was discussed. The results of modeling calculations give us the basis to understand that the schemes of description of the photochemical processes with participation of the excited particles do not now allow us to satisfactorily explain the results of experiments.

Characteristics of longitudinal variations of the ionosphere at the middle latitudes, obtained by observations of the satellite Interkosmos-19, were presented and discussed.

The Lomonosov MSU, Moscow, has presented results of optical and UV radiation observations, and also of streams of high-energy electrons obtained by the satellite "University Tatyana-2." The preliminary analysis has shown high correlation of UV and optical radiation in pulsations with duration of about 1 ms. It has been thus established that a correlation between the streams of high-energy electrons and UV or optical radiations is absent. It is noticed also that splashes in radiations are marked over cloudy sites of the Earth surface.

Although concentrations of aerosol particles in the atmosphere of the Earth are insignificant, it is however impossible to consider their influence on atmospheric conditions as negligibly small. It is enough to recollect the dramatic consequences of the "Eyjafjallajokull" volcanic eruption to Iceland and the smoke blanketing of the air of Central Russia and Siberia by summer fires. All these dramatic consequences grow from the influence of aerosol particles on the conditions of the air environment. There are no doubts that struggle against aerosol particles is one of the central foci of safe maintenance of the existence of all lives on Earth. Meanwhile, data on aerosol particles, the mechanisms of their occurrence, and their interaction with the environment and living organisms have remained unreliable until the present time.

Mechanisms of particle charging were discussed. This problem is important for safety maintenance during emergencies of atomic power stations and other nuclear power objects. The majority of radioactive aerosols are charged. The charged aerosols are also important in aerosol technology because motion of these particles can be controlled by means of external electromagnetic fields. The properties of carbon particles formed in the combustion process in airplane engines were also considered.

Electrochemical and Electromagnetic Phenomena in the Atmosphere Including Long-Lived and Plasma Objects

This section of the 2-nd International Symposium (AIS-2010) included Ball Lightning (ISBL-151) and the 4th International Symposium on Unconventional Plasmas (ISUP-4).

Work on these subjects that appeared during the past 2 years was reviewed. It has been noted that the practice of carrying out joint conferences on plasmoids, plasma structures, ball lightning, and unusual kinds of plasmas appears successful. Within the 2 years that have passed since the previous conference, intensive research on plasmoid physics plasma structures and BL was conducted, and experiments on realization of long-living plasma formations were made.

An activity shift was outlined in BL research to studying of lightning with an internal source of energy possessing a core and a cover and bearing noncompensated electrical charges.

The method of electric discharge in a closed volume in a polymeric tube with a small aperture has generated "fiery" spheres of some millimeters in diameter on exit from an aperture from this tube. It has appeared that the duration of their luminescence was of the order of 10 ms. As source material, metallic particles and some basalt were used.

Artificial BL, obtained by an explosion of nanostructured porous silicon that was impregnated by a solid oxidizer, potassium nitrate, was discussed. Luminescent spheres from 10 to 80 cm in diameter with a lifetime of about 1 s have been realized.

The influence of new kinds of plasma on the surface of combustible liquids was considered. Results of experiments on the influence of pulse and corona discharges on water (covered with a benzene layer), on kerosene, and also on alcohol and kerosene (covered with a layer of an aluminum powder) were presented.

Results of ongoing research of the Gatchina discharge with formation of large (up to 10 cm in diameter) luminescent objects over a volume with water were reported.

Results of research on the structure and evolution of stretched vortical plasmoids at the microwave discharge fed by the pulse and high-frequency generator were presented. It is revealed that the important role in formation of the stretched vortical plasmoid is played by a vibrational-translation relaxation of the excited molecules. Dusty plasmoids have been considered also. They are generated by means of the erosion plasma generator in which an aluminum powder is inserted into the discharge channel and the high-frequency Tesla generator is applied. It has thus appeared that typical lengths of created plasmoids range from 10 to 100 cm, and their characteristic time of life is about 1 s.

Results of research on erosive discharge characteristics change researches have been presented. To study the conditions of continuous existence of formed plasmoids and control of their spatial localization, research on generation of high-frequency discharges is carried out in gas streams. Thus were observed plasmoids in air streams at the exit from a spiral waveguide, and also at the exit from an aperture in a quartz tube located on its axis or in a lateral wall.

On the basis of experimental results on the influence of electric discharge plasma on various materials (including silicon oxide), the model of the following natural object formation is considered. It can be called BL. At the strike of the linear lightning into the earth (or a melting object of inorganic nature), an area of the melt is formed. At that point, plasma interaction reactions of thermal decomposition of hydrocarbon components, of soil, dust, and organic components and of drops of water to C and H_2 take place. In the field of heating, chemical reactions of oxide reduction to metals and metalloids occur, and pure powder particles (aluminum or silicon) and molecules CO_2 and H_2O appear. (This process is similar to the formation of powders at electric explosions of wires, or the precipitation of metal powders on a basis of oxides). The area appears to be unipolarly charged at the expense of the charge transferred to it from the linear lightning. So, an object in which the core consists of metal particles and gases, and a cover of fused oxide, is formed. The oxide layer decelerates metal particle oxidation by oxygen arriving from the outside. Inside the cavity there is a slow burning (metal or metalloid particles react with CO_2 and H_2O). Subsequently, an ejection of this object from the earth into air under the influence of gas pressure in the fulgurite areas takes place. Despite its possible large weight, it does not fall because of the Coulomb repulsion from the charged surface of the Earth. Internal reactions caused the object to be heated. The pressure inside the object rises, cracks in the cover appear, and it later scatters under the action of the Coulomb repulsion of charges.

It was shown that, within the limits of the already existing BL electrodynamic model, the energy density of an element of the energy core increases with downsizing of an element. The assumption of the existence of a "composite" object as a system of the tiny objects collected inside the general cover of a dielectric material allows us to explain cases of BL exit from sockets and their passage through small apertures and through intact glass.

Results of observation of radiowave interference in a waveguide of rectangular section were reported. Ceramic plates were located in Fibonacci chain order (quasiperiodic system) or the Cantor series (fractal system). From that it was studied what occurs at infringement of the order of the plate placement, shifting their parts for 1/3, 3/4, or 1/16 of the wavelength, respectively. In some cases, clicks of the electric breakdown in air were discovered in the waveguide; they lead to the occurrence of plasma structures.

A report that vorticity degree growth increases the stability of the atmospheric vortex lifetime was heard. For correct account of their formation mechanism, knowledge of the contribution to the formation process of the nonequilibrium self-consistent vortices structures of the storm cloud charged subsystems and research of their dynamics is necessary. Experimental data concerning high-altitude profiles of electric field specified the presence of strong electric fluctuations in storm clouds with characteristic sizes of 10–500 m. Electric field fluctuations on scales of $L \sim 10$–500 m (where L is the difference of the heights of two atmospheric layers), and also the presence of coherent electric structures, were discovered.

Combustion and Pollution: Environmental Impact

In the reports presented for this section, results of computation and experimental research directed toward the perfection of working processes in burner devices and internal combustion engines to provide maximum fuel economy and to lower the production of harmful substances (soot, NO, etc.) were discussed. Methods of burning and flame acceleration modeling in encumbered space and in pipes, methods of maintenance of fast transition of burning to detonation, and also methods of decreasing harmful substances at the burning of gas and liquid fuel, including safe recycling in an exhaust, were discussed.

Information Systems of Environmental Monitoring and Accident Prevention

In these reports, the following problems were considered: microdipole electromagnetic radiations (of slow-down character) induced by pulse X-ray or gamma sources; detection of the narrow directed pulse source of gamma quanta of high energy and the destructive influence of gamma radiation on electronic equipment; corrections of ionospheric delays at registration of the pulse signal, passing the ionosphere; and interrelation of errors of determination of coordinates and registration of arrival time in the range-difference method of a passive location.

It is shown that microdipole radiation, which spectrum is a pulse noise sending, lies in the field of low frequencies. The spectrum-correlation method is proposed for detection of the pulse sources of gamma quanta with time accumulation, allowing to allocate authentically the accepted radiation at a signal-to-noise ratio greater than two.

Rydberg radiation in the upper troposphere induced by the pulse sources of gamma quanta with energy of 1–3 MeV has been considered. It is shown that at pulse emission of 10^{22} gamma quanta radiation is reliably registered at distances of some hundreds of kilometers.

The question of the registration of electromagnetic radiation on board a space vehicle induced by the pulse sources of gamma quanta with duration of 10–100 ns and energy 1 MB was also considered.

On the basis of the presented reports, the Editorial board has prepared the following reviews for this book on important and interesting areas of atmosphere and ionosphere physics.

In Chap. 1 is discussed the contribution of excited atoms to the ionization processes under conditions of low-temperature plasma that may be regarded as a background for transformation of light excitation energy into electrical energy. Relevance of the dynamics chaos regime to the phenomenon of a diffusion autoionization within Rydberg quasi-molecular complexes is demonstrated, taking as an example collisions between Rydberg and normal alkali atoms. The presented data show the theoretical models of chemoionization processes, exploring “dipole-resonant mechanism” to be in satisfactory agreement with the experiment.

In Chap. 2 is presented a review of the theoretical status of the elementary atomic and molecular processes driven by strong monochromatic laser fields. The discussion is focused on near-threshold processes involving Rydberg intermediate states, which play an important role in the Earth’s upper atmosphere. The possibility of the stationary formalism of radiative scattering matrix, based on a renormalized Lippmann–Schwinger equation, is demonstrated. This approach provides a unified description of all near-threshold processes, where the transition amplitudes are represented by the radiative scattering matrix elements corresponding to all possible reaction channels. These processes include predissociation, associative ionization, exchange, and other reactions that cannot be described by the standard time-dependent models.

Chapter 3 is devoted to a number of chemical and photochemical processes in the atmosphere that are responsible for the formation of the tiniest (nanometric) aerosol particles which then increase to larger sizes by condensation and coagulation. Charging of aerosol particles is also of importance for the particle growth processes. Chapter 3 considers all the aforementioned aerosol processes, taking into account that the particle size is less or comparable to the mean free path of molecules in the carrier gas; that is, the molecular transport goes in either the free molecule or the transition regime. The chapter outlines an approach that permits strong simplifications in considering the aerosol processes in the transition regime. This approach forms a common basis for treating molecule, charge, and energy transport toward small aerosol particles.

In Chap. 4 are shown a few examples of the interpretation of experimental results in the upper atmosphere and ionosphere obtained by using the model of the upper atmosphere (UAM). In particular, the influence of the interplanetary magnetic field on the upper atmosphere and ionosphere during geomagnetic disturbances, as well as the problem of the "lithosphere–ionosphere connection," are examined. Numerical experiments allow a statistical description of the GPS TEC measurements, which are regarded as precursors of earthquakes. Ionospheric precursors to earthquakes calculated from the model showed satisfactory agreement between the UAM and the observations of GPS TEC. Guidelines are given for the detection of ionospheric precursors of earthquakes.

Chapter 5 is devoted to the theory analysis of the discharge phenomena called elves and sprites in the stratosphere and mesosphere initiated by tropospheric storm processes. At a quantitative level the process of redistribution of charges in an atmosphere at altitudes up to 150 km during the charging and discharging of a storm cloud is investigated. An important role of the small electric conductivity of the stratosphere and mesosphere is shown. At lightning discharge of a storm cloud, the area of the overcritical field appears under the ionosphere in which the avalanche ionization arises (elf). The account of the small electric conductivity of the atmosphere between the troposphere and the ionosphere has allowed explaining the long duration of discharge processes developing under the ionosphere, basically in the residual electrostatic polarization field.

Chapter 6 presents an experimental work that in essence is a continuation of a well-known work on microwave plasmoid physics carried out by the Nobel prize winner P.L. Kapitsa. The chapter is devoted to high-frequency (HF) plasmoid creation in low-temperature plasma, in swirl flows, which is of interest from the aspect of ball lightning (BL) physics and the creation of artificial ball lightning.

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Chapter 1
Ionization of Excited Atoms in Thermal Collisions

N.N. Bezuglov, Gennady V. Golubkov, and A.N. Klyucharev

Abstract This book is devoted to the modern theory and experimental investigations of the associative ionization (AI) reaction. The means of their further development are analyzed. Numerous applications in plasma chemistry, aeronomy, chemical physics of the upper atmosphere, and astrophysics have contributed to conducting this study. The threshold behavior of cross sections of the endothermic reaction AI is considered, and it is shown that the dependence of above-threshold energy E is a strictly linear in the quantum case, which differs substantially from the law $E^{3/2}$, resulting in a semiclassical theory. This result has a simple physical explanation because the matrix elements of scattering operator resulting from the tunneling effect are finite at $E = 0$. Comparison with the semiclassical theory has been made. A substantiation of the described possibility of elementary AI reaction dynamics in the diffusion approach is given. A detailed consideration of the applicability conditions of the "quantum chaos" theory for the spectrum of highly excited Rydberg molecules is carried out. A review of experimental studies of AI reaction under different conditions covering vapor cells, single effusive beams, two crossing beams, and cold matters (very briefly) is presented. The importance of accounting for specific distribution functions of atoms over a relative (colliding) velocity in AI rate constant evaluations is discussed, and a proper explanation of noticeable variations in experimental data is provided. Different types of colliding atomic/molecular pairs consisting of low-lying excited states (normal, metastable, and resonance) in inert and alkali gases are considered, and the corresponding futures of AI cross sections are analyzed. Experimental data on AI and Penning ionization processes involving the Rydberg states of hydrogen and alkali atoms

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are considered on the basis of a number of theoretical models. The relevance of diffusion motion of the optical electron through the Rydberg energy states toward the continuum resulting from appearance of the dynamics chaos regime in its evolution is demonstrated.

Keywords Metastable and Rydberg atoms • Ionization in slow atom collision • Intermediate Rydberg complex • Dynamics chaos

1.1 Introduction

Chemical ionization processes in the thermal and subthermal collisions of heavy particles with participation of the excited atoms are characterized by appreciable values of the reaction rate constants (Klyucharev and Vujnovic 1990; Klyucharev 1993). The universe at the initial stage of its existence was composed mainly of atoms, molecules, and positive and negative ions, containing $HD^{\pm}$, $LIH^{\pm}$, hydrogen, deuterium, helium, and lithium in their variety and different combinations. The results of recent spectroscopic observations of cosmic objects in the infrared range have shown the presence of anomalies, which appear in the disappearance of lines emitted by the hydrogen-like Rydberg atoms (RA) with values of the effective quantum number n_{eff} of the order of 10 (Gnedin et al. 2009). To this range, n_{eff} corresponds to the maximum on dependences of the RA chemical ionization processes $k(n_{\text{eff}})$ rate constants, i.e.:

$$X^{**}\left(n_{\text{eff}}\right) + Y \Rightarrow \begin{cases} XY^{+} + e^{-}, \\ X + Y^{+} + e^{-}, \\ X^{+} + Y + e^{-}. \end{cases} \tag{1.1}$$

When the concentration of neutral atoms is $c_{\text{A}} \sim 10^{17}\ \text{cm}^{-3}$ and the rate constant is $k \sim 10^{-9}\ \text{cm}^{3}\ \text{c}^{-1}$, the effective lifetime of RA is about $\tau_{\text{eff}}\ \ 10^{-8}$ s (note that for hydrogen RA with $n_{\text{eff}} = 10$, the table value gives $\tau_{\text{eff}} = 10^{-6}$ s).

The concept of low-temperature plasma physics includes sections of elementary processes and their applications. Interest in development in this direction, which first had appeared in the early twentieth century, not only has not declined but is constantly increasing. Now we can speak about the new field of “chemistry of plasma physics,” which is a junction of atomic and molecular collisions and chemistry of elementary gas-phase reactions leading to chemical transformations, including ionization and chemical ionization (Smirnov 1981). Studying the physics of ionization processes involving heavy particles, we have to consider the fundamental statements of atomic collision physics, which makes it possible to detect new phenomena and laws. One is the discovery of the new phenomenon of low-temperature plasma gas medium formation at its irradiation by light with wavelengths corresponding to resonant optical transitions in the atom (photoresonance plasma). Such plasma at the initial stage of its formation cannot be described within the traditional scheme of the gas discharge.

It is known that a direct analogy exists between the processes occurring in space and in laboratory facilities. For example, laboratory studies of laser-hydrogen plasma have shown that the features of the processes taking place in it are similar to the processes occurring in the atmosphere of cooling-type stars of the "white dwarf" class.

Recombination leading to filling of the Rydberg states, and being the main mechanism of the ionization-recombination processes with participation of the molecular ions, is sufficiently popular in the astrophysical literature. An example is low-temperature layers enriched by helium of those white dwarfs' atmosphere and the solar photosphere. At the same time, there remain many unresolved questions relating to the processes of a gas and a dust in the atmosphere of the satellite structures of the giant planet Jupiter: Io rich with sodium, where undoubtedly can take place the ionization processes involving excited sodium atoms, similar to those occurring in the laboratory photoresonance plasma in alkali metals vapors in Earth conditions (Klyucharev et al. 2007).

Recent results on the stochastic dynamics in the processes of chemical ionization (Klyucharev et al. 2010) in frames of the resonant collision model (Smirnov and Mihajlov 1971a) indicate the possibility of shifting the primary selective excitation of the RA over a group of excited states, and thereby of control of the elementary processes. The latter is of great interest, because it allows us to identify the relationship between determinism and stochasticity in atomic physics. Below we restrict ourselves to the effective principal quantum numbers $n_{\mathrm{eff}} \leq 25$, which provide the maximum effect of chemical ionization.

1.2 Collision of Atoms in the Thermal and Subthermal Energy Ranges Leading to Ionization

Depending on the state of particle-collision partners in the entrance and exit channels of reactions, the total set of ionization processes in collisions of atoms and molecules can be divided into the processes of collision ionization and chemical ionization. This is a conditional division, which is determined by the potential energy of the excitation and kinetic energy of relative motion of colliding particles. The range of kinetic energies of the atoms of interest to the physics of collision processes lies in the interval 10^{-9} to 10^{3} K, which extends from a "Bose–Einstein condensate" to high-current arc plasma. Remember that the energy of 8.617×10^{-5} eV corresponds to the temperature of 1 K, which agrees approximately with the temperature of liquid helium. Each interval of temperatures of the gas medium has its own set of preferred processes leading to the ionization; in this case, following the division of the collision energy E_{col} of relative motion: the thermal (10^{-1} to 1 eV), subthermal (10^{-3} to 10^{-1} eV), and cold (less than 10^{-3} eV), i.e., collisions in the experiments on laser cooling of atoms.

In the literature, the chemical ionization process is called the reaction in which the transition to a state of the ionization continuum is the result of the internal energy (excitation energy) of the colliding particles, and the energy of relative motion plays a minor role in energy balance. In other words, the energy of relative motion of atoms on the characteristic values of the inelastic transition distances in these reactions is much smaller than the ionization potential of the individual atoms partners. In connection with the development of new physical and technical trends in modern physics, such as the physics of active laser media, the interaction of radiation with matter is laser synthesis of chemical substances. Interest in these processes emerging in the past 60 years is markedly increased. However, available literature on the processes of ionization in slow atom–atom collisions in general relates to the reactions involving metastable atoms. The use of tunable dye lasers makes possible to implement a resonant optical excitation of atoms in the vast majority of elements, which markedly stimulated the experimental study of such processes. In this case, from energy considerations it follows that the ionization processes in slow symmetrical collisions are possible only if the pair collisions of resonantly excited atoms take place. At the same time two possibilities can be realized: (1) the doubled excitation energy is greater than the atom ionization potential, and (2) this energy is lower than that potential. The first case (1) takes place, for example, at the ionization of hydrogen and inert gases, halogens, nitrogen, and oxygen. The second one (2) is the ionization of alkali atoms of rare earth elements, uranium, most of the metal atoms, the ionization in collisions of metastable atoms of heavy inert gases with hydrogen.

As a result of the ionization process, in slow symmetrical and asymmetrical atom–atom collisions can be formed the following molecular and atomic ions:

$$\begin{array}{ll}\text{Symmetrical collision} & X(X^*) + X^* \to X_2^+ + e^- \\ \text{Asymmetrical collision} & X(X^*) + Y^* \to XY^+ + e^-\end{array} \tag{1.2}$$

$$\begin{array}{ll}\text{Symmetrical collision} & X\left(X^*\right) + X^* \to X^+ + X + e^- \\ \text{Asymmetrical collision} & X\left(X^*\right) + X^* \to X^+ + X + e^-\end{array} \tag{1.3}$$

or a pair of positive and negative ions

$$\begin{array}{ll}\text{Symmetrical collision} & X\left(X^*\right) + X^* \to X^+ + X^- \\ \text{Asymmetrical collision} & X\left(X^*\right) + Y^* \to X^+ + Y^-\end{array} \tag{1.4}$$

We do not consider here the processes of dissociative ionization and the ionization accompanied by a rearrangement of the particles, which can occur in atom–molecule collisions. Reactions (1.2, 1.3, and 1.4) differ by the process mechanisms. Reaction (1.2) is called associative ionization (AI). Note that reaction (1.3) in the cases where one partner is a metastable atom Y^* with the excitation energy exceeding the ionization potential of atom X is called the Penning ionization (PI).

The foregoing classification of the ionization processes in thermal collisions of atoms indicates only some of the possible reaction channels and in this sense is relative. For example, in the case of collisions of two highly excited atoms with the comparable ionization potential, six channels of reactions that lead to the formation of only atomic ions are theoretically possible:

$$\to \begin{cases} X^-\left(e_1^- e_2^-\right) + Y^+ \\ Y^-\left(e_1^- e_2^-\right) + X^+ \end{cases} \tag{1.5}$$

$$X^*\left(e_1^-\right) + Y^*\left(e_2^-\right) \Rightarrow \to \begin{cases} X^+ + Y\left(e_2^-\right) + e_1^- \\ X\left(e_1^-\right) + Y^+ + e_2^- \end{cases} \tag{1.6}$$

$$\to \begin{cases} X^+ + Y\left(e_1^-\right) + e_2^- \\ X\left(e_2^-\right) + Y^+ + e_1^- \end{cases} \tag{1.7}$$

In reactions (1.5, 1.6, and 1.7), the indices 1 and 2 refer to the optical electrons of atoms X and Y, respectively.

Quantitative conclusions about the effectiveness of chemical ionization with participation of emitting atoms in a broad range of binding energy of the optical electron by the end of the 1990s were possible primarily for alkali metal atoms (Klyucharev and Vujnovic 1990).

1.3 Basic Principles of the Theory

This section discusses the theory of collision ionization, which is characterized by a variety of methods and approaches developed during the past 20–30 years. We have skipped over those which by now have become generally accepted and widely used to describe various physical phenomena in atomic and molecular collisions and low-temperature plasmas and laser devices in the upper atmosphere and ionosphere, aeronomy, and astrophysics. However, many questions are yet to receive their final consideration.

1.3.1 Semiclassical Approach

If the excitation energy of the atom is greater than the ionization potential of the particle Y, then the Penning AI process proceeds. Then, for all the finite interatomic distances the quasi-molecule is found in the autoionizing states, decaying with the emission of an electron, and the formation of the molecular ion, if its existence is

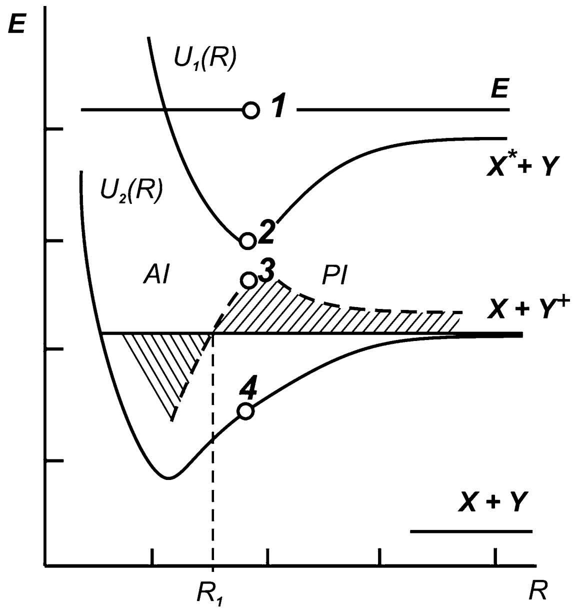

Fig. 1.1 Potential curves for the molecular ion $U_2(R)$ and the quasi-molecular system $U_1(R)$. The value E corresponds to the total energy of the system. The excitation energy of the atom Y^* is greater than the ionization potential of the atom X

possible. A diagram of the electron excited quasi-molecule XY^* potential curves and the ground state molecular ion XY^+, qualitatively illustrating a separation possibility of the processes

$$X^* + Y \to \begin{cases} XY^+ + e^- & \text{associative ionization (AI)} \quad (1.8) \\ X^+ + Y + e^- & n\text{–type Penning AI reaction (PI)} \quad (1.9) \end{cases}$$

(when the adiabatic approximation takes place), is shown in Fig. 1.1. An implementation of the Franck–Condon principle in the conservation of the nuclei energy is illustrated in this figure by presentation of the ordinate differences of points 1, 2 and 3, 4, respectively: $U_1(R) - U_2(R) = U_3(R) - U_4(R)$. When point 3 lies above the dissociation ion XY^+ limit, the PI channel is preferred. If an autoionization decay from the $U_1(R)$ term for the interatomic distances $R > R(1)$ takes place, the PI-type reaction with formation of the atomic ion and one electron happens (reaction (1.3)). Autoionization decay of $R < R(1)$ leads to the formation of the molecular ion in the stable vibrational excited state. In the same approximation, the energy of electrons releazed in the reaction channels at the interatomic distance R is equal to the $U_1(R) - U_2(R)$ difference. From analysis of the electron energy distribution in the reactions (1.2 and 1.3), we can judge not only about the relative efficiency of the molecular and atomic ion processes as the branching factor of the reaction, but also about the behavior of potential curves of the electronically excited molecules. The limiting value of the atoms (temperature) average energy, where the basic transition

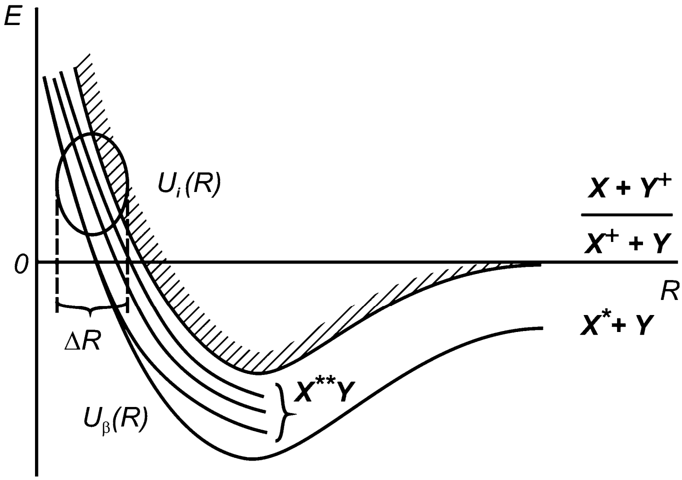

Fig. 1.2 Potential curves for the molecular ion XY^+ and the quasi-molecular XY^*. The excitation energy of the atom Y^* is smaller than the ionization potential of the atom X

preconditions do not violate, can be estimated from the ratio of the de Broglie wavelength of the atom and the characteristic atomic size, a_0. All this has led to the development of Penning electron spectroscopy as a new direction of experimental research.

If the excitation energy X^* is smaller than the Y ionization potential, than there are two possibilities: reaction (1.8) and (1.9) (in the diabatic representation). The first case takes place when the potential curves of the quasi-molecule U_β and the molecular ion U_i do not overlap (Fig. 1.2). In this case, the transition occurs because of the nonadiabatic coupling of the electron and nuclear motions in a wide range of interatomic distances ΔR, when they approach, and the potential curves of Rydberg states of the quasi-molecule $X^{**}Y$ are the Coulomb condensation. The second case corresponds to the situation when, in the vicinity of the point R_c, the potential curve XY^*, and the dissociative term (diabatic picture) intersects a set of curves of the Rydberg and ion U_i terms (Fig. 1.3). When going to the region of interatomic distances $R < R_\mathrm{c}$, the term XY^* becomes autoionization. Consequently, the reaction of the AI here is essentially a multichannel process, as occurs with the participation continuums of the Rydberg, dissociative, and ionized states (see Figs. 1.2, 1.3). As a result of the direct relationship of the Rydberg XY^{**}, the dissociative $X^* + Y$, the intermediate valence X^*Y, and the ionic X^+Y^- configurations, under the atom collisions are possible not only autoionization, but inelastic transitions, that can be accompanied with the increase (or decrease) of the initial atom excitation energies.

Analysis of the discrete level interaction with the states of the continuum and the infinite sequence of the Coulomb levels was carried out (Demkov and Komarov 1966). Strictly speaking, the problem of multiple transitions (associated with the

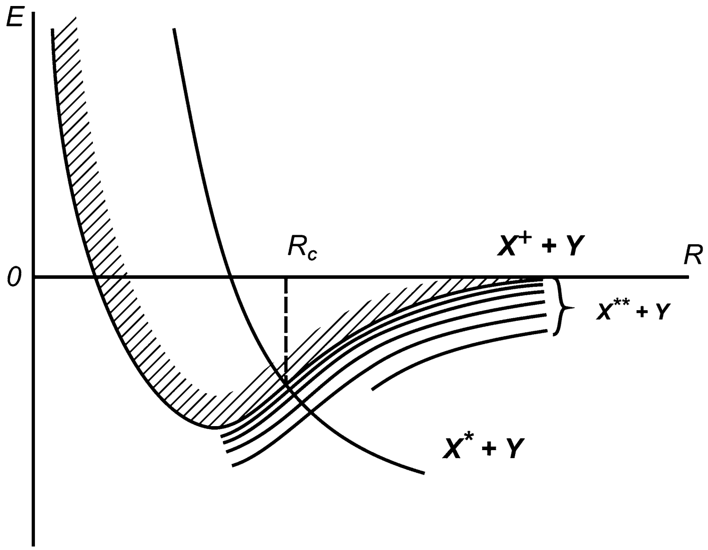

Fig. 1.3 The same as for Fig. 1.2 with a quasi-crossing of the potential curves in the point R_c

Coulomb refinement levels) is solved in the special model case, then the set of Rydberg terms is replaced by a system of the parallel lines, and the diabatic dissociative term is also linearized. In the framework of the Demkov–Osherov contour integral method (Demkov and Osherov 1968), the problem is reduced to multiplying the probabilities to stay on the dissociative term at each point of pseudo-crossing (followed by a summation of the exponents of all these points). This approach is reasonable if the ionization and the transitions to highly excited states are determined by the behavior of the system near the avoided crossing R_c in the small neighborhood L_R, which is the parameter of the problem. Upon reaching the point, $R = R_c$ of the bound state disappears, merging with a continuous spectrum. The ionization cross section in this approximation is equal to πR_c^2.

In the 1970s, the majority of model theoretical studies of the AI process were performed without a set of avoided crossings that occur right up to the potential curve of the quasi-molecule across the border of the molecular ion continuum. Attempts to take them into account in the framework of the traditional approaches based on individual review of each pseudo-crossing for highly excited states were not successful. In this regard, we developed a method that implements the "diffusion-based approach to the collision ionization of excited atoms" (Devdariani et al. 1988). We are talking about the diffusion over the quasi-molecule state energies in a single act of the collision: the main collision parameter is the binding energy of the excited electron. During the "diffusion," the initial single quasi-molecule term is transformed into a "burning" type of conic section at large distances ($R \to \infty$) with decrease in R (Fig. 1.4).

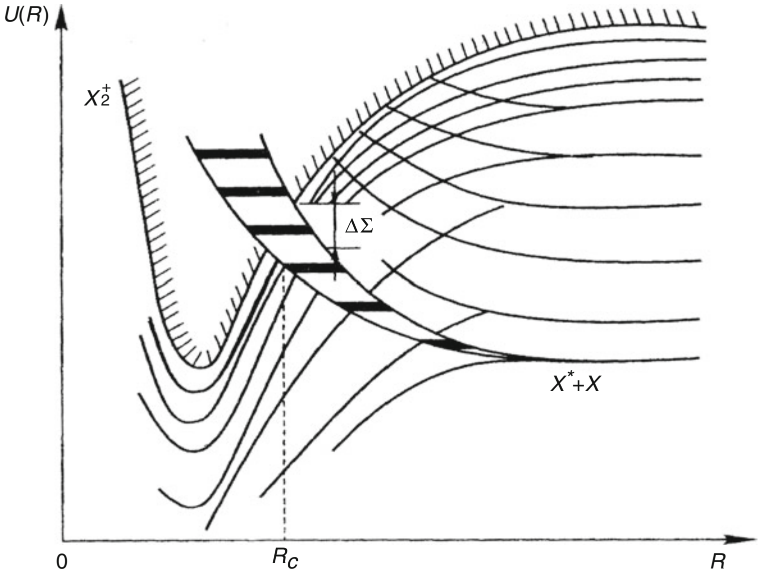

Fig. 1.4 Illustration of the quasi-crossing of covalent and ionic potential curves under the frame of the "diffusion" model

1.3.2 General Equations of the Scattering Theory

In presenting the formal scattering theory of atoms $\mathrm{X} + \mathrm{Y}^*$ with a transition to the final $\mathrm{e}^- + \mathrm{XY}^+$ state of the system, it is convenient to use a method of the multichannel quantum defect (MQD) (Golubkov and Ivanov 2001), which gives the most complete and consistent description of the resonant scattering and the reactions leading to the redistribution of particles. For simplicity, we exclude the valent $\mathrm{X}^*\mathrm{Y}^*$ and ionic $\mathrm{X}^+\mathrm{Y}^-$ configurations and represent the full Hamiltonian of the system under consideration in the form ($\hbar = m_\mathrm{e} = \mathrm{e} = 1$)

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}, \quad \mathbf{H}_0 = -\frac{1}{2}\boldsymbol{\Delta}_\mathbf{r} - \frac{1}{r} + \mathbf{H}_q, \tag{1.10}$$

where $-\frac{1}{2}\boldsymbol{\Delta}_\mathbf{r}$ is the operator of the kinetic energy of a weakly bonding electron, $\mathbf{r}$ is its coordinate read from the XY^+ ion center of mass, and $\mathbf{H}_\mathrm{q}$ is the molecular ion Hamiltonian dependent on the coordinate set $\{\mathbf{X}\}$ of the internal electrons (here, $q = \{v, N\}$ is the set of vibrational v and rotational N quantum numbers of the XY^+ ion). Note that the bound and autoionizing Rydberg states of the system belong to the configuration XY^{**} and differ only in sign (and magnitude) of the total energy E of the system, which can be conveniently measured from the ground state of the molecular ion.

The unperturbed Hamiltonian $\mathbf{H}_0$ for Rydberg channels is chosen in such a way that all interactions in the dissociative X + Y configurations are exactly taken into account, but in the scattering $e^- + XY^+$ channel only the Coulomb part $V^c = -\frac{1}{r}$ is contained. Thus, in the total Hamiltonian (Eq. 1.10), the operator $\mathbf{V} = \mathbf{V}^{nc} + \mathbf{V}^{CI}$ includes a non-Coulomb interaction of the electron with the ionic core $\mathbf{V}^{nc}$ and interaction $\mathbf{V}^{CI}$ responsible for the corresponding nonadiabatic transitions between $e^- + XY^+$ and $X^* + Y$ configurations.

A formal solution of the AI problem (or of the inverse process of the dissociative recombination) is reduced to define the collision $\mathbf{T}$–operator (related to the $\mathbf{S}$–matrix by the relationship $\mathbf{S} = \mathbf{1} - 2i\mathbf{T}$), which satisfies the system of the rearranged integral Lippman–Schwinger equations (Golubkov and Ivanov 2001):

$$\mathbf{T} = \mathbf{t} + \mathbf{t}(\mathbf{G} - \mathbf{G}_0)\mathbf{T}, \tag{1.11}$$

$$\mathbf{t} = \mathbf{V} + \mathbf{V}\mathbf{G}_0\mathbf{t}, \tag{1.12}$$

where $\mathbf{G} = (E - \mathbf{H}_0)^{-1}$ is the Green's operator with the interaction $\mathbf{V}$ turned off, and $\mathbf{G}_0$ is weakly dependent on the total energy E operator. We denote the basic wave functions of the unperturbed Hamiltonian $\mathbf{H}_0$ by $|q\rangle$ for the $e^- + XY^+$ configuration and $|\beta\rangle$ for the dissociative $X + Y^*$ configuration. The corresponding matrix elements $\langle q|\mathbf{T}|\beta\rangle$ are the amplitudes of the transitions $\alpha \Leftrightarrow \beta$ transitions that are symmetrical under permutation of the indices.

The Green's $\mathbf{G}$–operator in Eq. 1.11 is represented by the contribution of noninteracting $e^- + XY^+$ and $X^* + Y$ configurations and has the following form:

$$\mathbf{G}(E) = \sum_i |i\rangle \mathbf{G}^{(c)}(E - E_i)\langle i| + \frac{1}{\pi}\sum_\beta \int \frac{|\beta\rangle\langle\beta|}{E - E_\beta + i\gamma} \mathrm{d}E_\beta. \tag{1.13}$$

Here E_i and $|i\rangle$ are the excitation energies and corresponding wave functions of the XY^+ ion, and $\mathbf{G}^{(c)}$ is the Green function describing the electron motion in a Coloumb field. In the representation of spherical harmonics, it has the form

$$\mathbf{G}^{(c)}(\mathbf{r}, \mathbf{r}'; \varepsilon) = \sum_{lm} Y^*_{lm}\left(\frac{\mathbf{r}}{r}\right) G^{(c)}_l(r, r'; \varepsilon) Y_{lm}\left(\frac{\mathbf{r}'}{r'}\right),$$

where $Y_{lm}\left(\frac{\mathbf{r}}{r}\right)$ is the spherical function. It is important for further consideration that the radial function $G^{(c)}_l(r, r'; \varepsilon)$ can be separated into terms with weak and strong energy dependences (Demkov and Komarov 1966):

$$G^{(c)}_l\left(r, r'; \varepsilon\right) = \cot \pi\nu(\varepsilon)\, |\varphi_{\varepsilon l}(r)\rangle \left\langle \varphi_{\varepsilon l}\left(r'\right)\right| + g_l\left(r, r'; \varepsilon\right). \tag{1.14}$$

The first term in Eq. 1.14 reproduces the position of the Coulomb levels $\nu(\varepsilon) = (-2\varepsilon)^{-1/2}$ at $\varepsilon < 0$ and is expressed through the regular at-zero Coulomb wave functions $\varphi_{\varepsilon l}(r)$ normalized in accordance with

$$\langle \varphi_{\varepsilon l}(r) \, | \varphi_{\varepsilon' l}(r) \rangle = \pi \delta \left(\varepsilon - \varepsilon' \right).$$

After excluding the smoothed real part from (1.13):

$$\mathbf{G}_0(E) = \sum_{i,lm} |i\rangle Y_{lm}^* \left(\frac{\mathbf{r}}{r} \right) g_l \left(r, r'; E - E_i \right) Y_{lm} \left(\frac{\mathbf{r}'}{r'} \right) \langle i | + \frac{1}{\pi} \sum_{\beta} P \int \frac{|\beta\rangle \langle \beta|}{E - E_\beta} \mathrm{d}E_\beta$$

(P means the principal value of the integral), we can write the following equation for the collision **T**–operator:

$$\mathbf{T} = \mathbf{t} + \mathbf{t} \left\{ \sum_q |q\rangle \langle q| \cot \left[\pi \left(-2\varepsilon_q \right)^{-1/2} \right] - i \sum_\beta |\beta\rangle \langle \beta| \right\} \mathbf{T}. \tag{1.15}$$

Here $\varepsilon_q = E - E_q$ is the electron energy in the q-channel of motion, E_q is the energy of its vibrational and rotational excitation. For open channels $\left(\varepsilon_q > 0\right)$, the function $\cot \left[\pi \left(-2\varepsilon_q\right)^{-1/2}\right] = -i$.

Because of the linearity and the separable structure of the nucleus (which follows from the unique properties of the Coulomb Green function), the integral equation (1.15) reduces to a system of linear algebraic equations for the elements of **T**–matrix, in which the dissociative channels are taken into account along with the scattering channels, at the same time consistently ignoring the strong nonadiabatic coupling of the electronic and nuclear motions, which forms a heterogeneous continuum of intermediate Rydberg states interacting with the decaying dissociative terms (Golubkov et al. 1996a). These important properties follow from the formal scattering theory, and automatically provide a unitary **S**–matrix on an arbitrary basis, accounting for the movement of channels, which ensures the controlled precision of carried calculations.

1.3.3 Basic Wave Functions and Elements of Reaction t Matrix

Basic wave functions $|q\rangle$ in the Rydberg configuration (taking into account the vibrational and rotational motion of nuclei) are

$$|q\rangle = |JMlNv\rangle = \varphi_{\varepsilon_v l}(r) \varphi_i(\mathbf{x}) \chi_v^J(R) \Phi_{lN}^{JM} \left(\hat{r} \hat{R} \right). \tag{1.16}$$

Here φ_i is the electron wave function of the XY^+ ion, and $\chi_v^J(R)$ is the vibrational wavefunction. The total angular function of the system $\Phi_{lN}^{JM}(\hat{r}\hat{R})$ is defined in the representation with total angular momentum $\boldsymbol{J}$ and its projection $\boldsymbol{M}$, angular momentum N of the rotational notion of the nuclei, and in the case LS-coupling for σ configuration of XY^+ has the form (Golubkov and Ivanov 2001)

$$\Phi_{lN}^{JM}\left(\hat{r}\hat{R}\right) = \sum_m Y_{lm}(\hat{r})\, Y_{N,M-n}\left(\hat{R}\right)(lNmM-n\,|JM)$$

($\hat{r}$, and $\hat{R}$ are spherical coordinates of the electron and nucleus, and $(lNmM - n\,|JM)$ are the vector summation coefficients, $\boldsymbol{J} = \boldsymbol{l} + \boldsymbol{N}$). The $|q\rangle$ functions are determined in the laboratory frame of reference, where the direction of the z-axis coincides with the electron wave vector.

In the dissociative configuration the electrons are fast enough, so their motion is quantized in the field of the fixed nuclei and is described in the adiabatic approximation. For calculation of the configuration interaction matrix elements it is necessary to expand the channel wave functions (Eq. 1.16) into the adiabatic basis, that is, to pass into the coordinate system associated with the molecule, in which the absolute value of the projection of electronic angular momentum Λ on the molecular axis is fixed. States of a diatomic molecule in this basis are classified according to the values of J (the angular momentum of an electron l is not preserved in general). The total wave function in the adiabatic approximation is a superposition of the channel basis functions:

$$|JM\rho\Lambda v\rangle = \sum_l a_{l\rho}^{J\Lambda}\,|JMl\Lambda v\rangle\,. \tag{1.17}$$

Here ρ is the quantum number given by the largest coefficient of the expansion (1.17) characterizing the effective electron angular momentum of the Rydberg configuration with l mixing taken into account. The wave functions of the dissociative β configuration are determined quite similarly.

To calculate the elements $t_{lNv,l'N'v'}^{J}$ and $t_{lNv,l'\beta\Lambda}^{J}$ in the system of Eqs. 1.11 and 1.12 and responsible for the rovibronic and configuration nonadiabatic transitions, it is convenient to introduce the auxiliary $\bar{\mathbf{t}}$ operator, i.e.:

$$\bar{\mathbf{t}} = \mathbf{V} + \frac{1}{\pi}\sum_q P\int \mathbf{V}\frac{|q\rangle\,\langle q|}{E - E_q - \varepsilon}\bar{\mathbf{t}}\,\mathrm{d}\varepsilon$$

It describes the interaction of the electron with the ion core in an isolated Rydberg $e^- + XY^+$ configuration. Electron parts of matrix elements of the $\bar{\mathbf{t}}$–operator in the mixed basis (1.17), depending on R by definition, are diagonal with respect to subscripts ρ and Λ, and are expressed via the diabatic quantum defects $\bar{\mu}_{\rho\Lambda}$ as

$$\bar{t}_{\rho\Lambda,\rho'\Lambda'}^{J}(R) = -\tan\pi\,\bar{\mu}_{\rho\Lambda}(R)\delta_{\rho\rho'}\delta_{\Lambda\Lambda'}. \tag{1.18}$$

So long as the adiabatic basis $|JMl\Lambda v\rangle$ and channel basis (1.16) are connected by the unitary transformation (Golubkov et al. 1997)

$$|JMl\Lambda v\rangle = \sum_N U^{Jl}_{N\Lambda} \, |JMlNv\rangle \tag{1.19}$$

for $\bar{t}^J_{lNv,l'N'v'}$ elements we have

$$\bar{t}^J_{lNv,l'N'v'} = -\sum_{\rho\Lambda} a^{J\Lambda}_{l\rho} U^{Jl}_{N\Lambda} \times \left\langle \chi^J_v \right| \tan \pi \mu_{\rho\Lambda}(R) \left| \chi^J_{v'} \right\rangle a^{J\Lambda}_{\rho l'} U^{Jl'}_{\Lambda N'}, \tag{1.20}$$

where $U^{Jl}_{N\Lambda}$ is the Fano's rotation submatrix. Therefore, taking the pattern of Rydberg terms and the information about the adiabatic wave functions (1.17) as a basis, one can define by Eq. 1.20 a complete set of the $\bar{\mathbf{t}}$ matrix elements.

According to Eqs. 1.12 and 1.18, the reaction matrix $\mathbf{t}$ satisfies the operator equation

$$\mathbf{t} = \bar{\mathbf{t}} + \bar{\mathbf{t}} \frac{1}{\pi} \sum_\beta P \int \frac{|\beta\Lambda\rangle \, \langle\beta\Lambda|}{E - E_\beta} \mathbf{t} \, \mathrm{d}E_\beta.$$

From this equation with regard to the smallness of the configuration coupling, we can obtain the following expressions for the matrix elements:

$$t^J_{lNv,l'N'v'} = \bar{t}^J_{lNv,l'N'v'} + \frac{1}{\pi} \sum_\beta P \int \frac{V^{\mathrm{CI}}_{lNv,\beta\Lambda} V^{\mathrm{CI}}_{\beta\Lambda,l'N'v'}}{E - E_\beta} \mathrm{d}E_\beta, \tag{1.21}$$

$$t^J_{lNv,\beta\Lambda} = V^{\mathrm{CI}}_{lNv,\beta\Lambda} + \frac{1}{\pi} \sum_{l'N'v'} P \int \frac{\bar{t}^J_{lNv,l'N'v'} V^{\mathrm{CI}}_{l'N'v',\beta\Lambda}}{E - E_\beta} d\,E_\beta + \frac{1}{\pi} \sum_{\beta' \neq \beta, \Lambda'} P \int \frac{V^J_{lNv,\beta'\Lambda'} V^{\mathrm{CI}}_{\beta'\Lambda',\beta\Lambda}}{E - E_\beta} d\,E_\beta, \tag{1.22}$$

$$t^J_{\beta\Lambda,\beta'\Lambda'} = V^{\mathrm{CI}}_{\beta\Lambda,\beta'\Lambda'}. \tag{1.23}$$

The value of the CI is defined by specific peculiarities of the quasimolecule electron structure. The examples of well-known $\mathrm{e}^- + \mathrm{XY}^+$ systems show that it is really small, i.e., the values $\left| V^{\mathrm{CI}}_{lNv,\beta\Lambda} \right|^2$ are small in comparison with unity. Elements $t^J_{lNv,l'N'v'}$ in (1.21) are presented in the form of two terms, where the first one is caused by the interaction with the ion core and the second by the mixing of