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Collisions of Charged Particles with Molecules

等离子体中的分子过程

——带电粒子与分子的碰撞

（影印版）

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序　言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础，同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天，物理学不仅囿于基础科学和技术应用研究的范畴，而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到，改革开放三十多年来，随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展，我国物理学取得了跨越式的进步，做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下，近年来物理学相关书籍也呈现百花齐放的良好态势，在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看，尽管国内各出版社相继推出了一些质量很高的物理教材和图书，但系统总结物理学各门类知识和发展，深入浅出地介绍其与现代科学技术之间的渊源，并针对不同层次的读者提供有价值的教材和研究参考，仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展，特别是展现近年来中国物理学者的研究水平和成果，北京大学出版社在国家出版基金的支持下推出了“中外物理学精品书系”，试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家，确保了整套丛书的权威性和前瞻性。

这套书系内容丰富，涵盖面广，可读性强，其中既有对我国传统物理学发展的梳理和总结，也有对正在蓬勃发展的物理学前沿的全面展示；既引进和介绍了世界物理学研究的发展动态，也面向国际主流领域传播中国物理的优秀专著。可以说，“中外物理学精品书系”力图完整呈现近现代世界和中国物理

科学发展的全貌，是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

“中外物理学精品书系”另一个突出特点是，在把西方物理的精华要义“请进来”的同时，也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻，引进和翻译世界物理的经典著作和前沿动态，可以满足当前国内物理教学和科研工作的迫切需求。另一方面，改革开放几十年来，我国的物理学研究取得了长足发展，一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域，使世界对中国物理学的过去和现状有更多的深入了解，不仅充分展示出中国物理学研究和积累的“硬实力”，也向世界主动传播我国科技文化领域不断创新的“软实力”，对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是，“中外物理学精品书系”还对中国近现代物理学科的经典著作进行了全面收录。20 世纪以来，中国物理界诞生了很多经典作品，但当时大都分散出版，如今很多代表性的作品已经淹没在浩瀚的图书海洋中，读者们对这些论著也都是“只闻其声，未见其真”。该书系的编者们在这方面下了很大工夫，对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值，不仅可以很好地保护和传承我国物理学的经典文献，充分发挥其应有的传世育人的作用，更能使广大物理学人和青年学子切身体会我国物理学研究的发展脉络和优良传统，真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在 2006 年中国科学技术大会上指出，“加强基础研究是提升国家创新能力、积累智力资本的重要途径，是我国跻身世界科技强国的必要条件”。中国的发展在于创新，而基础研究正是一切创新的根本和源泉。我相信，这套“中外物理学精品书系”的出版，不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣，也将进一步推动其他相关基础科学更好更快地发展，为我国今后的科技创新和社会进步做出应有的贡献。

“中外物理学精品书系”编委会 主任

中国科学院院士，北京大学教授

王恩哥

2010 年 5 月于燕园

Y. Itikawa

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With 84 Figures

Springer

Preface

When I was a graduate student, I studied plasma physics. My thesis for D.Sc. was concerned with transport properties of plasmas. This study needed information of elementary collision processes in the plasma. Since the plasma considered was a fully ionized, hydrogen plasma, collisions were only the Coulomb scattering among plasma particles (i.e., electrons and protons). Therefore, no atomic physics was involved in the study. After my graduation, I started a theoretical study of atomic collisions. Among a variety of collision processes, I was particularly interested in electron–molecule collisions. Molecules are much more complicated than atoms. A detailed study of electron–molecule collisions was somewhat behind the study of electron–atom collisions. At first, my study of atomic collisions had no relation to plasma physics. Eventually, however, I realized that the electron–molecule collision is a fundamental elementary process in gaseous discharges. In fact, scientists engaged in the research of gaseous discharges, or more generally weakly ionized plasmas, are very much interested in electron–molecule collisions. I began to contact those scientists.

Then came an era of plasma processing. In the 1990s, a weakly ionized plasma found a wide range of applications. Requests of information of electron–molecule collisions and related subjects have arisen from industry. Personally, I have been asked to give a talk of atomic collisions to the community of application fields. They often want to have a text book on atomic collisions they can refer to. The present book is my answer to the request.

Many text books on plasma physics include sections for atomic collision processes, but usually they give only a general feature of the processes. On the other hand, many text books are available on the atomic and molecular collisions. Usually, however, they are too much detailed to be referred for application problems. This book has been written from the stand points of atomic physics. Nothing is mentioned about plasma physics. But the examples shown have been selected with an intension to the application in molecular plasmas. The description of atomic physics is as much compact as possible. But, if anyone wants to know more details, he/she is directed to a proper reference. In this sense, this book serves as a guide to atomic physics that is necessary to understand the molecular processes in plasmas. From the side of applications, the items sought after are cross-section data. Considering that situation, this book would also serve as a guide for cross-section data on molecular processes.

During the preparation of this book, many scientific colleagues in the world provided the results of their theoretical and experimental research on atomic collisions. I am very much grateful, particularly, to Professor H. Tanaka of the Sophia University, Tokyo. He not only made available the detailed results of the experiments of his group, but also kindly offered me technical help for the preparation of the manuscript.

Tokyo, March 2007 *Yukikazu Itikawa*

Contents

1 Introduction

Plasma is an ionized gas which contains equal amounts of positive and negative charges. Positive charges are carried by positive ions. Negative charges are usually supplied by electrons, but in some cases negative ions have a contribution. Plasmas are broadly classified into two classes. One is a high-temperature, fully ionized plasma. The other is a low-temperature, weakly ionized one. This book is concerned with a molecular plasma, i.e., a plasma containing neutral molecules. In most cases, a molecular plasma belongs to the class of low-temperature, weakly ionized plasmas. But, although belonging to the class, plasmas composed only of atoms (e.g., rare gases) are not dealt with in this book. Some of the high-temperature, fully ionized plasmas have a supply of molecules from outside and partly become a molecular plasma. For example, a plasma in a fusion device has a very hot core region, but also contains a large amount of molecules in its boundary region (see Sect. 2.4).

This book deals with molecular processes in the molecular plasmas. A molecular process literally means an elementary collision process involving molecules. In this book, however, it means a collision between charged particles (i.e., ions and electrons) and molecules. Electron collisions with molecular ions are also discussed in this book. Collisions involving only neutral molecules are primarily a subject of chemistry and less concerned with plasmas.

One of the typical examples of molecular plasmas is the ionosphere on the Earth and other planets. In the ionosphere, atoms and molecules are ionized mainly by the UV or X-ray photons from the Sun. Most regions of the Universe are in a state of plasmas. A stellar atmosphere, for example, is a kind of high-temperature plasmas, but molecules are often found there. Interstellar space is filled with very-low density matter. In the space, a clump of matter is found and called an interstellar cloud. Those clouds contain a variety of molecules. They also have ions and electrons. In that sense, the interstellar clouds are molecular plasmas. Although their fraction is very small, the charged particles play an important role in the interstellar cloud. Many of the laboratory plasmas are low-temperature, weakly ionized ones and generated from a molecular gas. In recent years, plasmas are utilized for a wide range of industrial purposes. Many of these plasmas are molecular. Fluorocarbon molecules, for instance, are used for plasma etching of microelectronics. Hydrocarbon molecules are the main ingredient of the plasma for the deposition of carbon layers. Atmospheric plasmas (i.e., plasmas generated from atmospheric gases) are widely used for pollution control or surface modification.

Molecular processes play fundamental roles in the plasmas. The production of positive ions (and free electrons) is of primary importance in generating and maintaining plasmas. An electron-impact ionization of molecules is the main process for that. In laboratory plasmas, electrons are accelerated by an applied electric field. On the other hand, those electrons lose their energy through collisions with plasma particles (mainly with molecules). As a result of balance of these two processes (i.e., acceleration and deceleration), the electrons have a stationary distribution of their energies. The resulting electron energy distribution function (EEDF) determines the transport properties of electrons and the rates of various electron–collision processes. In some cases (e.g., in the ionosphere), ions are produced by photoionization processes. The photoelectrons produced usually have a finite kinetic energy. Upon collisions with plasma particles, the photoelectrons degrade their energy to reach a thermal distribution of energies. The last, but not the least, important role of the molecular processes is the production of active species. Those products are ions, excited atoms and molecules, radicals, reactive atoms such as O and F, and high-energy photons. Some of the products even have a significant amount of kinetic energy (i.e., being "hot"). These species are the source of actions of practical importance.

The aim of this book is to list up all possible processes of collisions between charged particles (i.e., ions and electrons) and neutral molecules (and molecular ions). A brief description with figures of examples is given for each process. The descriptions are not too much detailed, but are intended to give an overall picture of the process. An emphasis is placed on the features which are tended unnoticed when the processes are considered for applications. Keeping in mind those collisions in a molecular plasma, discussions are concentrated on low-energy collisions. Collision energies considered are mostly in the range from thermal energy at room temperature (=0.026 eV) to 100 eV for electrons and to 10 eV for ions. For the understanding of the collision processes, the basic ideas and the fundamental quantities in the physics of atomic collisions are presented. Furthermore, specific features of molecular targets are summarized and a simple theory of electron–molecule collisions is given.

The plan of this book is as follows. Chapter 2 presents four examples of molecular plasmas: Earth's ionosphere (Sect. 2.1), interstellar clouds (Sect. 2.2), gaseous discharges (mainly for plasma processing) (Sect. 2.3), and edge plasmas in fusion devices (Sect. 2.4). Chapters 3 and 4 give the fundamental ideas and quantities in the physics of atomic collisions and, in particular, a brief theory of electron–molecule collisions. These are the minimum essence of the atomic collision physics, necessary for understanding the molecular processes described in the following chapters. Chapter 5 is devoted to the electron–molecule collision processes. Seven different processes are stated separately. Four related subjects (i.e., the total scattering, momentum–transfer, emission, and stopping cross-sections) are also described in additional sections. Most of the collision processes described in this chapter are those for the target molecules in their ground state. In the practical applications, the information is needed about the collisions involving targets in excited states. Those information are scarcely available. The situation is summarized in the last section of Chap. 5. Next chapter (Chap. 6) deals with ion collisions with molecules. The ion–molecule collisions are much more complicated than the electron–molecule ones. Besides the same processes as in the electron–molecule collisions, charge changing processes and rearrangement of atomic components are possible in the ion–molecule collisions. The description of the ion–molecule collisions are broadly divided into three parts: momentum-transfer processes (Sect. 6.2), inelastic collisions with no change of collision system (Sect. 6.3), and rearrangements, including charge changing processes (Sect. 6.4). Chapter 7 briefly reviews the electron collisions with molecular ions. This process is not necessarily major in molecular plasmas, but has a special feature as a collision of two charged particles. After the description of the general feature of the electron collisions with molecular ions, recombination processes are separately described in Sect. 7.2. To make this book more informative, useful tables and a guide for cross-section data are attached as appendices. Appendix A gives tables showing magnitudes of typical macroscopic quantities derived from cross-sections. Appendix B tabulates molecular parameters needed to understand the cross-section data. A simple theory of cross-section calculation is the Born approximation. It is not necessarily accurate, but very useful to analyze the physics under the collision process. Appendix C presents how to use the Born approximation, particularly for the electron-impact excitation of rotational and vibrational states of a molecule. For the demonstration of the variety of electron–molecule collisions, Appendix D graphically shows sets of cross-sections for four simple molecules (H_2, N_2, H_2O, and CO_2). The last three appendices (Appendices E, F, and G) are a guide to readers who want to find cross-section data. It is not a complete guide, but gives a clue when they search necessary data.

A few important collision processes in molecular plasmas or related phenomena are out of the scope of this book. In a weakly ionized plasma, collisions among neutral particles (i.e., molecule–molecule collisions) may have as much a significance as the collisions involving charged particles. In particular, collisions of active neutral species (particularly, radicals and excited molecules) with other molecules often play a decisive role for plasma activity in applications. Those neutral–neutral collisions are too complicated to summarize in a chapter or two and hence totally excluded from this book. Another processes not mentioned here are the elementary processes on the surface of the apparatus or electrodes. The surface processes are sensitively dependent on the condition of the surface. It is difficult to state those processes without specifying the surface conditions.

In this book, many examples of cross-sections are shown graphically or tabulated. These examples are primarily presented to show the general feature of the respective processes. Although they have been carefully selected as reliable data, they are not necessarily the best (i.e., the most accurate) values for applications. In other words, this book is not a compilation of cross-section data. This would, however, serve as a guide to find and understand the cross-section data.

2

Plasmas Involving Molecules

2.1 Ionosphere

A part of the atmosphere of the Earth and other planets is ionized by solar radiation and precipitating particles from outside. The part of rather high density of electrons is called an ionosphere. This is a typical example of molecular plasmas in nature. Here we consider the ionosphere on the Earth. For the ionospheres on the other planets, as well as details of the Earth's ionosphere, see the text book of Schunk and Nagy [144].

The Earth's ionosphere is located at the height of 60–1,000 km. The structure of the ionosphere is different for the day side and night side (more precisely, depending on the local time). It is severely affected by the solar activity. Figure 2.1 shows one example of ionic composition and electron density of the day side ionosphere at the minimum of solar activity [85]. This is a composite picture based on a few rocket and satellite measurements in 1963 and 1964. The absolute value of ion number density is normalized to the electron number density measured separately. Typical value of the electron density is $\sim 10^5\,\mathrm{cm}^{-3}$ at 100 km and $\sim 10^6\,\mathrm{cm}^{-3}$ at 200 km. These values are compared with the density of atmosphere: $\sim 10^{13}\,\mathrm{cm}^{-3}$ at 100 km and $\sim 10^{10}\,\mathrm{cm}^{-3}$ at 200 km. In the region of ionosphere, the Earth's atmosphere is composed mainly of N_2, O_2, and O. Above about 200 km, atomic oxygen dominates over the molecular components.

In the day side region at the height of about 100 km, the ionospheric plasma is maintained in the following manner:

(1) Ionization by solar radiation, particularly by the radiation of short wavelength

$$\text{Solar radiation} + N_2 \rightarrow N_2^+ + e(\text{ph})$$

$$\text{Solar radiation} + O_2 \rightarrow O_2^+ + e(\text{ph})$$