# Atomic Inner-Shell Processes

BERND CRASEMANN

VOLUME I

## Ionization and Transition Probabilities

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# Preface

Interest in the physics of atomic inner shells is currently undergoing a renaissance after lying nearly dormant for some forty years. Basic problems that had at one time been set aside as intractable can now be solved with modern experimental and theoretical techniques. Impetus is lent to the effort by the importance of applications to space science, surface studies, plasma physics, and other areas of practical concern.

The present volumes have been structured as a treatise in order to reflect the current status of this rapidly expanding field of research. Beyond serving as a reference work, it can thus be used as a guide for scientists who plan to enter this area of research.

Volume I deals with ionization and transition probabilities. The authors of the eleven chapters in this volume discuss inner-shell excitation by electrons, heavy charged particles, and photons, as well as atomic excitation accompanying nuclear decay. The theory of radiative and radiationless transitions is surveyed, both in terms of single-particle descriptions and of more complex many-body approaches. The very recent advances in the theory of multiple decay processes are summarized. The difficult subject of the calculation of transition energies is discussed, and energy shifts caused by the chemical environment and hyperfine interactions are surveyed.

In Volume II, experimental aspects of the field are covered, including a summary of the use of radioactive atoms for studies of atomic transition probabilities, and surveys of modern techniques of electron and photon spectrometry. Selected practical applications of inner-shell processes are outlined.

The subject of these volumes cuts across traditional scientific disciplines. It overlaps with areas of x-ray, atomic, and nuclear physics, astrophysics, chemistry, surface and materials science, and the engineering of radiation shields. We hope that these volumes will be useful for research workers in these various fields and for scientists who wish to become familiar with new areas of the subject.

As editor, I have had the privilege of working on this enterprise with friends and colleagues in several countries. I am grateful for their patience and cooperation throughout the lengthy and difficult effort. I am indebted to Dr. Melvin S. Freedman, of the Argonne National Laboratory, for advice on Chapter 5, and I wish to express special thanks to my co-worker

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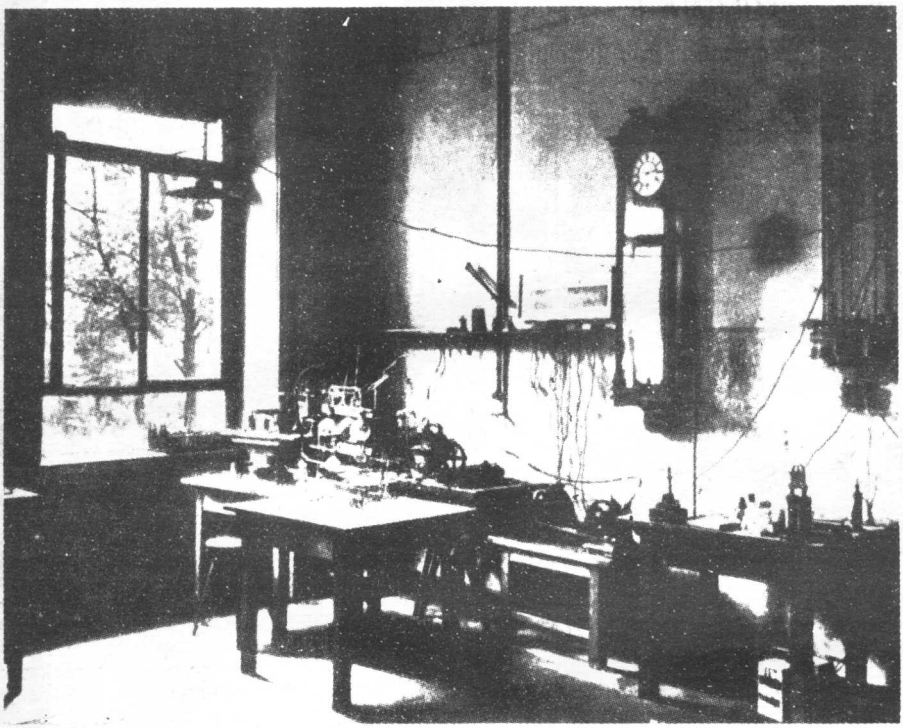

Where it all started: Röntgen's chambers in the Physical Institute of the University, Würzburg, where x rays were discovered in 1895. The photograph, made in 1923, is from Otto Glasser, "Wilhelm Conrad Röntgen und die Geschichte der Röntgenstrahlen," Springer-Verlag, Berlin, 1931. (Reprinted with permission.)

# Contents

# 1

# Theory of Charged-Particle Excitation

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## 1.1. Introduction

Since the early days of Bohr's theory of the atom, photon spectroscopy of characteristic x rays has been cultivated because the inner-shell processes involved are easily interpreted in terms of radiative one-electron transitions between hydrogenlike atomic states. Similarly, the interaction of swiftly moving charged particles with inner-shell electrons occupies a distinctive place in collision spectroscopy. It is our objective to show that relatively simple theoretical concepts can explain the characteristics of deep inelastic atomic collisions which result in the production of inner-shell vacancies.

In this chapter, we attempt to give a systematic exposition of the collision mechanisms which govern inner-shell vacancy production by electrons, bare charged heavy particles (protons, alpha particles, etc.), and complex heavy ions. The collision energies of greatest interest lie in the keV and MeV range. We have indicated the relation between the different approaches that have been applied to these problems, but we have organized the material from the viewpoint with which we are most conversant. This has meant that we have given more space to quantum mechanical collision theory, both in the Born and semiclassical versions, and less space to the details of classical and binary encounter models. Most quantitative theoretical work on the inner-shell excitation mechanism has so far dealt with direct Coulomb ionization; we have therefore given this process the greatest weight. We have, however, presented a general semiclassical formalism for treating inelastic collisions between ions and atoms and have shown how this formalism can be applied to the quasi-molecular electron promotion model, which has proved fruitful in the interpretation of low-velocity ion–atom collisions. In an effort to stress the unifying features of different excitation mechanisms, we have also shown how transition probabilities for Coulomb excitation and ionization, or for Coulomb-induced charge transfer, may be derived from the general formalism.

Although we have surveyed our subject broadly, our list of references is representative rather than complete. Fortunately, several excellent reviews are available to complement our account (Massey *et al.*, 1969; Mohr, 1968; Garcia *et al.*, 1973; Kessel and Fastrup, 1973). A useful source for further orientation is that of Fink *et al.* (1973).

A word on units is in order. Although it is tempting to use atomic units in a review of this kind, we have preferred to retain greater flexibility for making comparisons between our equations and those appearing in the literature, old and new. Except where otherwise indicated, we have adopted an unrationalized system of units in which Planck's constant has the value $\hbar = 1$. The Bohr radius of the hydrogen atom is thus $a_0 = (me^2)^{-1}$, where $m$ denotes the electron mass. The velocity of the electron in this Bohr orbit is $v_0 = e^2$. For the heavy-ion physicist, we note that $v_0$ corresponds to an energy of $\sim$25 keV/amu. The Rydberg energy is defined as $R_\infty = me^4/2$. We have used $M_1$ for projectile mass and $M_2$ for target mass; $Z_1e$ and $Z_2e$ denote the effective charges of the projectile and the target nucleus.

## 1.2. Born Approximation

Consider a scattering problem in which an incident projectile of velocity $v$, charge $Z_1e$, and mass $M_1$ collides with a stationary atom of mass $M_2$ in some initial state $i$, usually the ground state. The projectile (which may be traveling at relativistic or nonrelativistic velocities) thereby imparts some of its energy to the atom and leaves the atom in some arbitrary final state $f$. If an inner shell is ionized by the collision, the final state will be described as a vacancy in the inner shell of the atom and as an electron emitted with finite kinetic energy into the continuum.

The scattering will be viewed from a coordinate system centered on the atom. In this relative coordinate frame, the initial velocity $v$ corresponds to the laboratory velocity, since the atom is initially at rest. However, due to the recoil of the atom, the final velocity in this frame will not be the laboratory velocity. For the case of incident electrons, the center of mass frame, laboratory frame, and relative frame will all approximately coincide.

### *1.2.1. Arbitrary Projectiles*

For the moment, we shall assume that the incident projectile is distinguishable from the atomic electrons. The special exchange problems associated with incident electrons will be treated in Sec. 1.2.2. If the total Hamiltonian describing the scattering system is expressed as $H = H_0 + V$, the transition amplitude from an initial state $i$ to a final state $f$ is given by

$$T_{fi} = \langle \Phi_f \mid V \mid \Psi \rangle, \tag{1}$$

where

$$H_0 \Phi_f = E_f \Phi_f ,$$

and where $\Psi$ is the wave function for the total Hamiltonian $H$. Equation (1) is a particularly convenient starting point for a theoretical calculation if $H_0$ is chosen such that the interaction $V$ represents a small perturbation which vanishes as the separation between projectile and atom increases.

Most of the theoretical studies of atomic inner-shell ionization by electron impact have used Eq. (1) as a starting point. There has been, however, some interest in using a classical picture to describe the scattering process (cf. Gryzinski, 1959, 1965). In this picture, the scattering is viewed as a classical binary collision between the incident electron and an atomic electron. Calculations of this type have been applied more extensively to electron-impact excitation and ionization of outer-shell electrons than to inner-shell electrons. Here, we shall deal primarily with the quantum mechanical description of the collision process, but semiclassical methods will be discussed in Secs. 1.4 and 1.5 for the heavy-particle collisions.

Since the exact wave function $\Psi$ cannot be determined even for scattering from the simplest atoms, a practical application of Eq. (1) involves choosing $H_0$ and approximating $\Psi$. All the quantal calculations for inner-shell ionization to this point have chosen $H_0$ to be the sum of the Hamiltonian for the atom, $H_A$, and the Hamiltonian for the free motion of the impinging projectile, $H_p$,

$$H_0 = H_A(\xi) + H_p(\mathbf{r}_p). \tag{2}$$

Here $\xi$ represents the coordinates for all the atomic electrons and $\mathbf{r}_p$ is the coordinate of the projectile. With this choice for $H_0$, $\Phi_f$ can be expressed in terms of products of eigenfunctions of $H_A$ and $H_p$. A particular set of eigenfunctions for the field free operator $H_p$ is given by the plane-wave solutions

$$\phi_{\mathbf{K}_f}(p) = (2\pi)^{-3/2} \mathsf{U}_{\sigma_p}(\mathbf{K}_f) \exp(i\mathbf{K}_f \cdot \mathbf{r}_p), \tag{3}$$

where $\mathsf{U}_{\sigma_p}$ is the projectile spin wave function and $\mathbf{K}_f$ is the final momentum. If Eq. (3) describes a nonrelativistic electron, $\mathsf{U}$ represents a two-component Pauli spinor. If the projectile has relativistic energies, $\mathsf{U}$ represents a four-component Dirac spinor. The Dirac spinor for a free particle has been given by Darwin (1928).

For the final state of the system, the atomic Hamiltonian $H_A$ describes $N - 1$ bound electrons and one unbound electron. The eigenfunctions $\psi$ of $H_A$ are also known, at least in principle. Ideally, one could hope to use properly antisymmetrized self-consistent (relativistic or nonrelativistic) Hartree–Fock wave functions to describe the atom plus ejected electron. While such a description of the atomic electrons is presently feasible, calculations have used less sophisticated wave functions. Typically, in an independent-electron model of the atom, the atomic wave functions are

assumed to be represented by product wave functions and the ejected atomic electron is chosen to be moving in some effective Coulomb field or, even less realistically, it is sometimes described by a plane wave. It should be kept in mind that inaccuracies in the eigenfunctions of $H_A$ can obscure the effects of later approximations.

Since the choice of $H_0$ in principle determines $\Phi_f$ and $V$, an appropriate approximation for the exact wave function $\Psi$ would make possible the evaluation of the transition amplitude Eq. (1). In the spirit of first-order perturbation theory, all quantal calculations of inner-shell ionization have so far approximated $\Psi$ to be an initial-state eigenfunction of $H_0$. Since the projectile wave function is thus a plane wave both initially and finally, this approximation is the well-known (plane-wave) Born approximation, which has received considerable attention in the literature (cf. Merzbacher and Lewis, 1958; Inokuti, 1971). The primary assumption underlying the Born approximation is that the Coulomb distortion of the projectile wave function is small. This assumption has received some experimental vindication for inner-shell ionization by electron impact from the work of Hansen *et al.* (1964) and Hansen and Flammersfeld (1966). These experiments measured cross sections for $K$-shell ionization of medium-to-heavy elements by impact of electrons and positrons. If the projectile wave function was strongly distorted by the Coulomb interaction, one would expect the cross sections for electrons and positrons to be very different. The experimental cross sections for electrons and positrons, however, were found to agree to within the experimental error of 10 to 20% for incident energies in the range 0.1–1.4 MeV.

The Born approximation transition amplitude is

$$T_{fi}^{\mathrm{B}} = (2\pi)^{-3} \int \psi_f^*(\xi)\, \mathsf{U}_{\sigma_p'}{}^*(\mathbf{K}_f)\, V(\xi, \sigma_\xi, \mathbf{r}_p, \sigma_p) \times \mathsf{U}_{\sigma_p}(\mathbf{K}_i)\psi_i(\xi)\, \exp(i\mathbf{q}\cdot\mathbf{r}_p)\, d^3r_p\, d^3\xi, \tag{4}$$

where $\mathbf{q} = \mathbf{K}_i - \mathbf{K}_f$, and $d^3\xi$ represents integration over the coordinates of all the atomic electrons. It should be noted that the interaction potential depends on the spins of the projectile and target electrons. The form of the interaction potential $V$ must be known before any further reduction of Eq. (4) can be made. In the interest of obtaining results that can be applied to both relativistic and nonrelativistic scattering, we adopt for $V$ the general form

$$V(\xi, \sigma_\xi, \mathbf{r}_p, \sigma_p) = V_c(\mathbf{r}_p, \sigma_p) + \sum_{j=1}^{N} V_{jp}(\mathbf{r}_j, \sigma_j, \mathbf{r}_p, \sigma_p), \tag{5}$$

where

$$V_{jp} = (Z_1 e^2/|\mathbf{r}_p - \mathbf{r}_j|) F(\sigma_j, \sigma_p) \exp(i\lambda |\mathbf{r}_p - \mathbf{r}_j|). \tag{5a}$$

Here $Z_1$ is the charge of the projectile. The interaction potential for nonrelativistic spin-independent scattering can be obtained from Eq. (5) by setting $\lambda = 0$, $F = 1$, and $V_c$ equal to the Coulomb interaction between the projectile and the atomic nucleus.

Insertion of Eq. (5) into Eq. (4) gives the Born amplitude in terms of the $N$-particle antisymmetric atomic wave functions and interactions. This amplitude can be reduced to integrations over single-particle wave functions as follows: As has been previously noted, $\psi$ is an eigenfunction of the $N$-particle Hamiltonian $H_A$. We then make the following assumptions about $\psi$:

1. $\psi$ can be expressed as a properly antisymmetrized combination of products of single-particle wave functions (e.g., a Slater determinant);
2. the single-particle wave functions of the nonparticipating atomic electrons are unchanged by the ionizing collision;
3. the single-particle bound and continuum wave functions of the ejected electron are orthogonal to each other and to all the other bound atomic wave functions.

It is to be noted that these assumptions about the atomic wave functions are not part of the Born approximation. To treat effects of correlations or different angular momentum coupling schemes properly, one would have to form linear combinations of wave functions of this type.

From the orthogonality requirement 3, it can be seen immediately that the matrix elements of the first term $V_c$ of the interaction potential Eq. (5) must vanish, since it has no dependence on the atomic coordinates. [This happy circumstance is also the cause of some of the major difficulties associated with the Born approximation (Madison and Shelton, 1973).] The matrix element of the two-body interaction can be simplified by integration over $\mathbf{r}_p$:

$$T_{fi}^{\mathrm{B}} = -[Z_1 e^2/2\pi^2(q^2 - \lambda^2)] \int \psi_f^*(\xi)\, \mathsf{U}_{\sigma_p'}{}^*(\mathbf{K}_f) \times \sum_{j=1}^{N} F(\sigma_j, \sigma_p) \exp(i\mathbf{q}\cdot\mathbf{r}_j)\, \mathsf{U}_{\sigma_p}(\mathbf{K}_i)\psi_i(\xi)\, d^3\xi. \tag{6}$$

If $A(1, \ldots, N)$ is the idempotent operator that antisymmetrizes wave functions for $N$ identical particles, the antisymmetric atomic wave function can be expressed in terms of single-particle wave functions $\chi_i$ as follows:

$$\psi_f(\xi) = (N!)^{1/2} A(1, \ldots, N)\chi_f(1)\chi_2(2)\cdots\chi_N(N). \tag{7}$$